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Note

Gas chromatographic–mass spectrometric method for the quantitative analysis of carbofuran in water

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Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methyl carbamate) is a broad spectrum insecticide/nematicide[1]. A variety of analytical methods involving gas chromatography (GC)[2–5] and high-performance liquid chromatography[6–9] have been reported for the analysis of carbofuran in environmental matrices. All these methods have varying degrees of specificity. We sought a reliable quantitative method with a high degree of specificity for confirmation of low-level carbofuran residues in water samples involved in various environmental monitoring programs. This paper reports a rapid specific method which allows accurate quantitation of carbofuran in water at the 10 μg/l level, with a lower limit of detection of 0.5–1 μg/l.

EXPERIMENTAL

All solvents employed were Baker (Phillipsburgh, NJ, U.S.A.) Resi-Analyzed®. Standards were analytical grade (>99% purity) prepared in FMC laboratories.

Gas chromatography–mass spectrometry

A Hewlett-Packard HP5992B microprocessor controlled GC–mass spectrometry (MS) system was used. The system was equipped with a 122 cm × 2 mm I.D. silanized glass column packed with Tenax GC 60–80 mesh. The GC–MS system included a HP5990B quadrapole mass spectrometer coupled to a HP9825 computer and a HP9885 flexible disk. Operating conditions were: column temperature, 260°C; injector temperature, 260°C; carrier gas, helium (20 ml/min); ion source, 170°C; electron impact energy, 70 eV; electron multiplier voltage, 2.8 eV.

Methodology

Extraction. Water samples (100 g) were acidified by the addition of three drops of concentrated hydrochloric acid. The acid solution was extracted twice with 150 ml dichloromethane (DCM).

Conversion of carbofuran to 2,3-dihydro-2,2-dimethyl-7-hydroxybenzofuran (7-phenol). The DCM extract was washed twice with 150 ml 0.5 *N* sodium hydroxide and the aqueous phase discarded. The DCM was reduced in volume to *ca.* 10 ml using a Kuderna–Danish (KD) evaporative concentrator on a steam bath. The extract was

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taken just to dryness with a gentle stream of nitrogen. A 25-ml volume of 0.5 *N* NaOH was added to the residue and the solution stirred 0.5 hours at room temperature. The contents of the flask were washed two times with 50 ml DCM and the DCM discarded. The basic hydrolysis solution was made acidic by the addition of 5 ml concentrated hydrochloric acid and the solution extracted twice with 50 ml DCM. The DCM extract was dried by filtration through anhydrous sodium sulfate. The filter pad was rinsed with an additional 25 ml DCM. The combined extracts were placed in a KD concentrator and 50 ml methanol and five drops of diethylene glycol (as a keeper) were added. The solution was reduced in volume to *ca.* 5 ml on a stream bath and quantitatively transferred to a graduated centrifuge tube with methanol. The methanolic extract was reduced in volume to exactly 1 ml under a gentle stream of nitrogen for analysis.

Quantitation. Quantitation was accomplished by comparing the area of abundance at the 164 ion (molecular ion of 7-phenol) in a sample to that of a standard injection of a known quantity of 7-phenol (typically 1 ng).

The following formula was employed

$$\text{ppm} = \frac{\text{area of unknown} \times \text{ng standard}}{\text{area of standard} \times \text{mg water injected}} \times \text{CF}$$

where CF = 1.35; the molecular weight ratio of carbofuran (221) to 7-phenol (164).

The detection system was shown to be linear over the 0.25–2.0 ng range. A standard injection was made after each sample and the average of all standards was used to calculate μg/l values. An indication of the precision of calculation is the coefficient of error (standard deviation/mean) observed for the alternate standard injections (typically six standard injections). The coefficient of error ranged from 0.03–0.07 in the work reported.

Sensitivity. Method sensitivity (quantitatively reliable measurement of re-

TABLE I

RECOVERY OF CARBOFURAN FROM FORTIFIED WATER SAMPLES

Sample number	*Fortification level (μg/l)*	*Recovery level (μg/l)*	*Recovery (%)*
1	10	6.1	61.0
2	10	6.3	63.0
3	10	7.3	73.0
4	10	6.9	69.0
5	20	12.9	64.5
6	30	24.5	81.6
7	30	23.8	79.3
8	40	32.0	80.0
9	40	29.9	74.7
10	50	46.1	92.2
		Average	73.8
		Standard deviation	9.8

TABLE II

MASS MAJOR FRAGMENTS OF CARBOFURAN AND 7-PHENOL

Ion	*Carbofuran (relative abundance)*	*7-Phenol (relative abundance)*
221	10	–
165	12	12
164	100	100
149	63	76
147	9	11
131	18	30
123	16	26
122	17	25
121	11	20
103	9	14

sponse) was validated down to the 10 μg/l level by satisfactory recovery of carbofuran (as 7-phenol) from artificially fortified control samples. Method detectability, recognition of MS detector response was possible at 0.1 ng injected on column (0.7 μg/l).

RESULTS AND DISCUSSION

Table I lists the recoveries obtained from fortification experiments.

The conversion of carbofuran to 7-phenol was incorporated into the method for two reasons: first 7-phenol ionizes at 70 eV approximately five times as well as

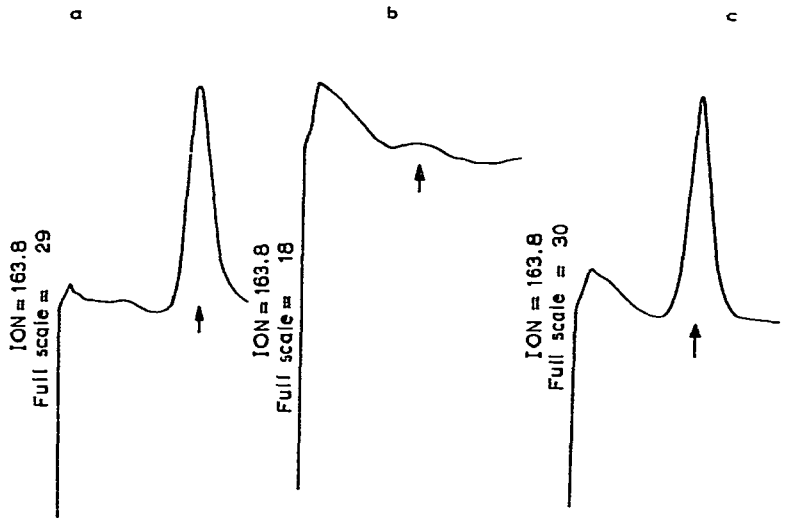

Fig. 1. Typical chromatograms from the analysis of carbofuran in water. a, 1 ng 7-phenol, area = 2341 units (scale = 29 abundance units); b, control water sample 200 mg injected (scale = 18 abundance units); c, control water sample fortified with 10 μg/l carbofuran 200 mg injected, area = 2384 units (scale = 30 abundance units). Response is equivalent to 6.9 μg/l carbofuran.

carbofuran. This is evidenced by comparison of mass to total ion abundance for each compound. Carbofuran gives essentially the same mass spectra as 7-phenol (see Table II); second the conversion allows one to take advantage of 7-phenol's acidity for sample cleanup. The initial base wash removes acidic coextractives while the DCM wash of the hydrolyzed mixture removes neutral and basic coextractives. This simple acid–base partition provides all the sample cleanup required for the analysis.

Control experiments demonstrated the quantitative nature of the hydrolysis of carbofuran to 7-phenol. It was also possible to demonstrate that the 7-phenol anion was unextractable from the basic hydrolysis mixture. Finally, control experiments showed that base wash of the initial DCM extract did not remove any carbofuran while it removed 7-phenol quantitatively.

Fig. 1 shows typical selected ion chromatograms derived through this method.

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