The accuracy of the method is shown in Table III.

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Determination of Benomyl by Reversed-Phase Liquid Chromatography

Gunter Zweig*[1] and Ru-yu Gao[2]

Sanitary Engineering and Environmental Health Research Laboratory, University of California, Richmond Field Station, Richmond, California 94804

In support of the field research being conducted by this laboratory on the exposure to pesticides by fruit and crop harvesters, it became necessary to develop an analytical method for the fungicide benomyl (methyl [1-[(butylamino)-carbonyl]-1*H*-benzimidazol-2-yl]carbamate). Because these field studies generated a large number of samples, the requirements for the proposed analytical scheme were speed and simplicity without sacrificing accuracy. Since the matrixes to be analyzed were relatively devoid of interferences (cotton gloves, surgical patches, and plant leaf surfaces), elaborate cleanup steps would probably not be needed.

Analytical methods for benomyl and its metabolite carbendazim have been recently reviewed (*1*). Kirkland (*2*) and Bleidner (*3*) in their scheme converted benomyl in soil and plant tissues to carbendazim by acid treatment and analyzed carbendazim by HPLC on a strong cation-exchange column. Chiba and Veres (*4*) distinguished between carbendazim and benomyl by first converting carbendazim to the corresponding *n*-propylcarbamoyl derivative with *n*-propyl isocyanate (PIC) at low temperatures and stabilizing benomyl by the addition of *n*-butyl isocyanate (BIC). They then resolved the resultant mixture by HPLC on a silica gel column.

Farrow et al. (*5*) recognized the instability of benomyl in organic solvents and recommended refluxing plant and fruit extracts with HCl, thereby causing the quantitative conversion of benomyl to carbendazim. The latter was analyzed by HPLC on silica gel or reversed-phase HPLC on an ODS column. Cabras and co-workers (*6*) reported on the separation of carbendazim and benomyl from other fungicides by reversed-phase HPLC but apparently did not recognize the instability of benomyl in organic solvents.

The method which will be described here is based on the discovery by Chiba et al. (*4*, *7*, *8*) that benomyl is converted to carbendazim in many organic solvents to varying degrees of completion. Of the solvents they studied, ethanol, dioxane, and methanol effected the conversion to carbendazim to 92% or greater. Quantitative conversion in methanol was achieved in 5.6 h. As will be shown in this paper, acetonitrile is a suitable solvent for the extraction of benomyl and carbendazim from cotton gauze and foliage and, at the same time, an effective solvent for the rapid quantitative conversion of benomyl to carbendazim, reaching completion in 1 to 3 h depending on temperature.

EXPERIMENTAL SECTION

Materials. Authentic samples of benomyl and carbendazim were obtained from the EPA Reference Standard Repository, Research Triangle Park, NC; carbendazim was also obtained from the Agrichemicals Department, E. I. du Pont de Nemours & Co.

All solvents used throughout were HPLC grade ("Baker Analyzed" or equivalent). Water for HPLC solvents were first passed through a Milli-Q water purification system. Mobile-phase solvents were further purified and degassed by filtering them through a Millipore filter in vacuo just prior to use.

High-Performance Liquid Chromatography Apparatus. Waters Model 6000A solvent delivery system; WISP automatic sample processor; Waters Data Module with Automatic Integrator; Model 450 variable wavelength detector; RP-18 Spheri 5, Brownlee Labs. bonded reversed-phase column (25 cm × 2 mm, i.d.).

Ultraviolet Spectrophotometer. Spectronic 2000, Bausch & Lomb.

Analytical Scheme for Benomyl and Carbendazim. Standard solutions of benomyl (2 μg/mL to 12 μg/mL) and carbendazim (1.3 μg/mL to 7.9 μg/mL) are prepared in acetonitrile. Fresh solutions of benomyl are kept at room temperature for 3 h or 40 °C for 1 h before use. This waiting period can be decreased even further, because the benomyl-to-carbendazim

[1] Visiting Scholar from the U.S. Environmental Protection Agency, Washington, DC.
[2] Visiting Scientist from Nankai University, Tianjin, People's Republic of China.

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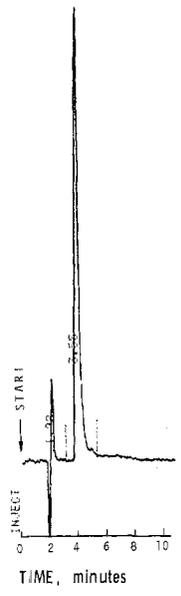

Figure 1. Reversed-phase HPLC chromatogram of 10 ppm of benomyl in solution: kept at room temperature for 3 h; 25 μL injected into C-18 bonded reversed-phase column; mobile phase, acetonitrile–water (50:50 (v/v)); other experimental details in text. Retention time of "aged" benomyl is identical with that of authentic carbendazim in acetonitrile solution, 3.55 min.

conversion begins immediately upon the addition of an organic extracting solvent to a sample. However, the prescribed waiting period of 3 h at room temperature prior to HPLC analysis assures that the reaction has indeed gone to completion.

Standard curves are prepared by injecting 25-μL aliquots of the standard solutions into the HPLC column. Chromatography is performed with acetonitrile–water (50:50 (v/v) as mobile phase, maintaining a flow rate of 1.5 mL/min. Carbendazim is detected at 286 nm with a retention time of 3.5 min (see Figure 1). Benomyl can be stabilized in acetonitrile solution by the addition of excess *n*-butyl isocyanate (1000:1 (w/w)) (7) and chromatographed as benomyl by HPLC under the same experimental conditions. A single, well resolved peak elutes at 15.8 min. Areas underneath the curves are automatically integrated and averaged, and a response factor (area/ng) is calculated. The minimum detectable quantities for carbendazim and benomyl are 5 and 7.5 ng, respectively, based on the smallest area quantifiable by the automatic integrator. Precision for duplicate runs is 1% or better.

Unknown samples are analyzed as carbendazim by the same methods as described above for standards, and concentrations are automatically calculated by the Data Module using the latest response factor for carbendazim standards which are interspersed between every five samples (i.e., every tenth run, since all samples are analyzed in duplicates). A variability of retention time ±10% during an 8-h workday has been observed but has no appreciable effect on the response factor.

All results are expressed as concentration of benomyl. If carbendazim is used as standard, the conversion factor of 1.52 is applied.

Surgical gauze patches (3 × 3 in.), used as dermal dosimeters in field studies on pesticide dermal exposure by farm workers, were dosed with known amounts of carbendazim ranging from 5.1 to 102 μg and stabilized benomyl (127.5 and 255.0 μg) (7). These and untreated patches were extracted with 30.0 or 60.0 mL of acetonitrile in 125-mL wide-mouth LPE-bottles with screw cap closure by shaking on a mechanical platform at about 200 Hz for 1 h. The extracts were filtered through Millipore BD (0.6 μm), and 50- to 200-μL aliquots were analyzed for carbendazim and benomyl by HPLC. Prior to HPLC analysis, extracts were allowed to stand at room temperature for 3 h or warmed to 40 °C for 1 h so that the benomyl → carbendazim reaction in the absence of *n*-butyl isocyanate would have gone to completion.

RESULTS

Kinetics of Reaction. In order to demonstrate that the conversion of benomyl to carbendazim in acetonitrile solution occurs spontaneously and quantitatively, advantage is taken of a strong absorption maximum of benomyl at 292.6 nm. As carbendazim is formed, this peak disappears and changes to a shoulder, while a new peak at 280.1 nm is formed. Both benomyl and carbendazim have an additional peak at 286.1 nm.

Table I. Molar Absorptivity of Benomyl and Carbendazim in Acetonitrile

compound	molar absorptivity[a] 292.6 nm	286.1 nm	280.1 nm
benomyl[b]	21 587	17 928	14 079[c]
carbendazim	3 313[d]	12 924	11 985

[a] Average of two experiments. [b] Stabilized by the addition of *n*-butyl isocyanate. [c] No peak or shoulder. [d] Shoulder only.

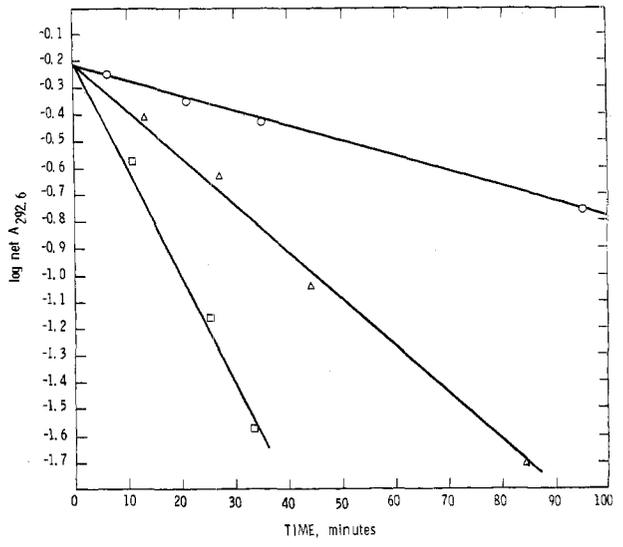

Figure 2. Semilog plot of "time" (min) vs. "log net absorbance" at 292.6 nm of solution of benomyl in acetonitrile at three different temperatures: 21.3; 30.0; 40.0 °C.

Molar absorptivities for benomyl and carbendazim, dissolved in acetonitrile, were determined and are listed in Table I. The molar absorptivity of benomyl was obtained by stabilizing benomyl in solution by the addition of an excess (1000:1, by weight) of *n*-butyl isocyanate (7). In this way, the equilibrium of the reaction benomyl → carbendazim + BIC is shifted to the left and in effect stabilizes benomyl in many organic solvents indefinitely.

A kinetic study of the simultaneous degradation of benomyl to carbendazim in acetonitrile was undertaken at three different temperatures. About 2.52 mg of benomyl was dissolved in 250.0 mL of acetonitrile at room temperature. Five minutes after the addition of the solvent, aliquots of this solution were placed in 125-mL Erlenmeyer flasks and shaken with reciprocal motion in constant temperature baths at 21.3, 30.0, and 40.0 °C. At timed intervals, thereafter, the absorbance of these solutions was measured at 292.6 nm, and the results were plotted as semilog functions (see Figure 2). "Observed" absorbance is corrected for absorbance at equilibrium to yield "net" absorbance, which is plotted. This correction is necessary to account for the low absorbance at this wavelength due to carbendazim. As is seen in Figure 2, the plots at three temperatures result in straight lines with a negative slope, demonstrating first-order kinetics for this reaction.

Rate constants were calculated from the straight lines, shown in Figure 2, and are listed in Table II. A plot of log k vs. $1/T$ resulted in a straight line as predicted from the

Table II. Rate Constants of the Reaction Benomyl to Carbendazim at Three Temperatures

temp, °C	rate constant (k), A min^{-1}	temp coefficient
21.3	−0.0060	3.35[a]
30.0	−0.0175	2.33
40.0	−0.0390	

[a] Adjusted for $\Delta t = 10$.

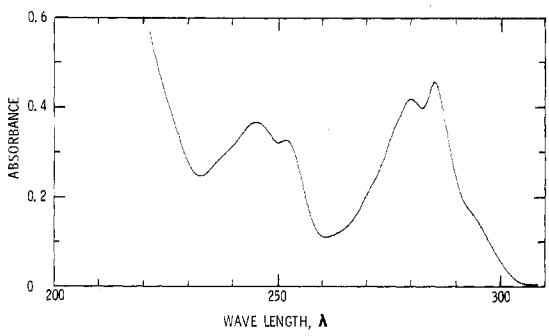

Figure 3. UV spectrum of 8.19 ppm solution of benomyl in acetonitrile kept at room temperature for 3 h; the resultant spectrum is identical with that of 5.65 ppm carbendazim dissolved in acetonitrile.

Arrhenius equation, thus demonstrating the positive effect of temperature on reaction velocity. The temperature coefficients for the reaction between 21.3 and 40.0 °C were found to be above 2 per Δ10 °C as may be seen from Table II. A value of 2 to 3 has been observed for most homogeneous processes.

Quantitative Formation of Carbendazim. In order to validate the analytical method for benomyl (that is the analysis of carbendazim), it was necessary to demonstrate the quantitative conversion of benomyl to carbendazim under the stated experimental conditions. This could be shown by two methods:

The first of these methods is the spectrophotometric analysis of benomyl in acetonitrile at the end of the reaction. A weighed amount of benomyl was dissolved in 100 mL of acetonitrile (8.19 ppm) and the absorbance measured at 292.6 nm at room temperature. When the absorbance had reached a constant value over a 10-min period, the reaction was considered as having gone to completion. The time required for this to happen was between 2 and 3 h at room temperature. From the absorbance of this solution at 280.1 nm and 286.1 nm and the corresponding molar absorptivities, the final concentration of carbendazim was calculated and found to be 5.65 ppm. This demonstrated that the reaction from benomyl to carbendazim was quantitative (104% yield). The UV spectrum of the resultant solution was identical with that of carbendazim and is shown in Figure 3.

In the second method, acetonitrile solutions containing weighed amounts of benomyl were allowed to reach equilibrium (3 h at room temperature or 1 h at 40 °C). Aliquots of these solutions at equilibrium were then analyzed for carbendazim by HPLC as described above. In one such experiment, 11.38 ppm of benomyl yielded 7.39 ppm of carbendazim, and in a second experiment 9.13 ppm of benomyl resulted in 6.01 ppm of carbendazim. The calculated concentrations of carbendazim for these two benomyl solutions were 7.50 ppm and 6.02 ppm, respectively, demonstrating again that the reaction is quantitative.

Recoveries of Added Carbendazim and Benomyl As shown in Table III, recoveries of added carbendazim were in the range of 87.0–100.4%. Untreated patches yielded no detectable residues or any extraneous interferences in the chromatography.

Table III. Recovery Study of Carbendazim and Benomyl from Surgical Gauze Patches

sample no.	compound	amt, μg added	amt, μg found	% recovery
1-3-5	carbendazim	102.00	96.12	94.2
1-3-5′	carbendazim	102.00	97.08	95.2
1-3-6	carbendazim	102.00	92.80	91.1
1-3-6′	carbendazim	102.00	97.40	95.5
1-3-7	carbendazim	51.00	48.60	95.3
1-3-7′	carbendazim	51.00	50.40	98.8
1-3-8	carbendazim	51.00	49.55	97.2
1-3-8′	carbendazim	51.00	51.20	100.4
1-3-11	carbendazim	10.20	10.02	98.3
1-3-11′	carbendazim	10.20	9.27	90.9
1-3-11″	carbendazim	10.20	9.53	93.5
1-3-12	carbendazim	5.10	4.43	87.0
1-3-12′	carbendazim	5.10	4.77	93.4
1-3-12″	carbendazim	5.10	4.95	96.8
1-3-13	benomyl[a]	127.5	126.6	99.3
1-3-13′	benomyl	127.5	125.0	98.0
1-3-14	benomyl	255.0	252.2	98.9
1-3-14′	benomyl	255.0	250.0	98.0

[a] Benomyl was stabilized by the addition of excess n-butyl isocyanate (1000:1 (w/w)).

DISCUSSION

It is recognized that the analytical method proposed for benomyl, in effect, determines the concentration of carbendazim, the degradation product of benomyl. If one were to stabilize benomyl with n-butyl isocyanate, as proposed by Chiba (*7*), all of the naturally formed carbendazim would also be converted to benomyl, and the results would be an expression of "total benomyl". The hitherto recommended residue methods for benomyl involve the acid treatment of extracts in order to convert all residues to carbendazim. The method described here represents a considerable simplification over the other methods by taking advantage of the spontaneous and quantitative conversion of benomyl to carbendazim in acetonitrile without any other chemical treatment. The practical implications are that any analytical procedure for benomyl which involves extraction with an organic solvent will result in partial or complete conversion to carbendazim before the determinative step in the analytical scheme has been reached. By using acetonitrile and observing a finite waiting period, one is now assured of the quantitative conversion to carbendazim. An added advantage of the present method is the utilization of commercially available reversed-phase HPLC columns and the use of a simple isocratic mobile phase.

This method has been applied with excellent results in a detailed study of dermal exposure to benomyl by strawberry harvesters in California (*9*, *10*).

Registry No. Benomyl, 17804-35-2.

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Reduction of Gas Chromatographic Needle Volatilization and Septum Bleed with Active Septum Cooling

James F. Pankow,* William E. Asher, and Lorne M. Isabelle

Department of Envronmental Science, Oregon Graduate Center, 19600 N.W. Walker Road, Beaverton, Oregon 97006

Gas chromatographic analyses requiring high injector port temperatures often display peaks due to septum bleed. In a temperature-programmed chromatogram these effects may be observed as discrete "ghost" peaks and/or base line drift. Both of these effects hinder the analytical procedure and lead to such problems as reduced sensitivity, unreliable integration of peaks, and difficulty in peak identification. It is therefore desirable to eliminate or at least minimize septum bleed.

This phenomenon has been studied by several researchers and is caused by the emission of short-chained silicone polymers, degradation products from the septum, and materials sorbed into the septum during manufacture and storage (*1–10*). As a result, bleed levels rise as the injector temperature is raised. Early methods of minimizing bleed consisted of conditioning septa with heat either in vacuo or under a flow of inert gas (N_2, He) (*1–3*) or by solvent extraction (*3, 4*). Septa faced with Teflon, aluminum, polyimide, or asbestos have also been used (*5*). Methods which do not involve septum modifications employ specialized septum holders. The "septum swinger" of Purcell et al. (*6*) placed the septum in a sliding metal mounting so that the septum could be swung away from the front of the injector immediately after the injection. Current models of capillary column gas chromatographs provide septum sweep (*7*). This reduces bleed by flushing it from the injector before it can reach the head of the column. It also prevents compounds sorbed into the septum during the injection from finding their way onto the column. Older packed column instruments may be retrofitted with commercially available septum sweep injector heads. Tucknott and Williams (*8*) passively cooled the septum by means of an extended, finned septum holder constructed of brass and stainless steel. A similar device made from Teflon was developed by Smith et al. (*9*). In addition to minimizing septum bleed, cooling the septum will reduce volatilization of compounds from the needle. This is an advantage since such volatilization causes variability in the amounts of analytes placed on the column as well as a tendency for discrimination against the less volatile components. Grob and Grob (*11*) have discussed how injection techniques may be used to minimize such effects.

The disadvantage of conditioning a septum with heat or by solvent extraction is that its usable lifetime is reduced. Teflon-faced septa do not eliminate bleed once the coating has been pierced. Septum sweep is effective in reducing bleed, but since the septum still remains hot, variable volatilization can still affect the method precision. On this basis, it is desirable to investigate whether maintaining a septum at low temperatures by active cooling can simultaneously (1) reduce septum bleed and (2) improve method precision. Such improvements will be of use in both packed and capillary column gas chromatography.

EXPERIMENTAL SECTION

A prototype septum cooler (Model SC-1, Figure 1) and septa (Type F-232-C) were obtained from Canton Bio-Medical Products (Boulder, CO). The former was made available by the manufacturer for trial use. It operates by expanding liquid CO_2 through a pinhole orifice into a brass cooling tube which is in contact with the septum. The septa were Teflon-faced and were specially designed for use with the septum cooler. CO_2 for the septum cooler was from a standard CO_2 cylinder equipped with a siphon dip tube. The gas flow at the vent of the septum cooler was 2.3 L/min at a current cost of approximately 0.1 U.S. dollars/h. The following alkane standard was prepared as a test mixture (compound number, name (concentration in ng/μL)): 1, octadecane (38); 2, nonadecane (42); 3, eicosane (49); 4, docosane (50); 5, tetracosane (53); 6, octacosane (67); 7, dotriacontane (74); 8, tetratriacontane (77); and 9, hexatriacontane (82). The standard was prepared in distilled glass grade hexane obtained from Burdick and Jackson (Muskegon, MI). The alkanes were obtained from Chemical Sample Co. (Columbus, OH) in 99% purity.

The gas chromatograph (GC) used was a Perkin-Elmer 900 (Perkin Elmer Co., Norwalk, CT) equipped with a flame ionization detector (FID). In the case of the experiments with the septum cooler, a standard Perkin-Elmer 900 injector was bored out to an inside diameter of 6.4 mm so that the front *unpacked* portion of the 2 mm i.d., 6.4 mm o.d. glass column could serve directly as the glass liner. The 2-m portion of the column which extended into the oven was packed with 1.5% OV-101 on Supelcoport (Supelco, Bellefonte, PA). The carrier gas was N_2 at a flow of 25 mL/min. The H_2 and air flows to the FID were 25 mL/min and 250 mL/min, respectively.

A second injector was modified for septum sweep to allow a comparative evaluation of the septum cooler. This injector was bored out to an inside diameter of 6.4 mm, and a septum sweep gas vent line was installed midway between the carrier gas inlet and the front end of the injector (i.e., 1.25 cm from the front end of the injector). The column was installed to within 2.5 cm of the front end of the injector. A 2.5 cm long, 1.6 mm i.d. stainless steel insert was placed between the end of the column and the front end of the injector. The column end of the insert was notched to permit passage of carrier gas. To sweep septum bleed from the injector, a 1.0 mm deep circular groove and a 1.6 mm i.d. hole (halfway through) were placed in the insert at a position directly opposite the new sweep vent line. A needle valve was placed on the sweep vent line and adjusted to 1.0 mL/min. The same type of septa used in the septum cooler were used with this injector. A three-finned aluminum septum nut was used to hold the septum in place.

We desired to evaluate the septum cooler in terms of its beneficial effects in reducing variable volatilization from the needle as it pierces the septum. Therefore, all injections were performed by using the "in-needle" method since that method will tend to exacerbate such variability (*11*). The precision of the results obtained may therefore be interpreted as approximate lower limits of what is obtainable with the septum cooler. Peak areas were recorded by a Hewlett-Packard (Avondale, PA) 3390A integrator. The following GC temperature program was employed: hold at

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