TABLE 1

SUMMARY OF FUNGICIDAL AND NEMATICIDAL DOSAGE LEVEL RANGES FOR *trans*-1,4-DIBROMOBUTENE-2* IN FRESNO SANDY LOAM SOIL (MOISTURE EQUIVALENT 8.0–10.0%)

Pathogen	Control criterion	Dosage level ranges of dibromobutene within which complete or nearly complete fungicidal or nematicidal control effects were obtained				
		Gallon crocks	Greenhouse benches and ground beds		Field plots	
		Complete soil mix (g/gal of soil)	Surface treatment (g/sq ft)	Complete soil mix (g/cu ft)	Surface treatment (lbs/ac)	Mixed to 6-in. depth (lbs/ac)
Meloidogyne sp.	Root knot on tomatoes	.05–0.2†	> 2.0‡	1.0–2.0†	> 200	> 200
Heterodera schactii	Infestation of sugar-beet roots	0.2 –0.4†	—	2.0–3.0	—	—
Sclerotium rolfsii	Viability of sclerotia	.07–0.2†	1.0–2.0†	2.0–4.0†	100–200†	150–200†
Pythium ultimum	Damping-off of seedlings	—	0.5–2.0†	0.5–2.0†	50–100	50–100
Rhizoctonia solani	Basal stem rot of beans	—	0.5–1.0†	—	—	—
Fusarium-Pythium complex	Seedling rot and blight of peas	—	—	0.5–3.0	—	—

* Applied as a 10–20% w dust in talc. Dosage levels are given in g or lbs of active ingredient.
† Complete control or complete fungicidal and nematicidal effect in range.
‡ > indicates inadequate to no control at highest dosage used.

the chemical was spread with a garden rake, and for deeper applications in the field an Ariens-Tiller was employed.

In some instances fungicidal effects were determined by plating out exposed fungal spores and mycelium, but in the majority of cases control effects were measured by freedom of disease shown by host test plants. Table 1, therefore, summarizes briefly the results of numerous trials to determine the effectiveness of *trans*-1,4-dibromobutene-2 as a soil fumigant.

In tests on *Heterodera schactii, Meloidogyne* sp., *Pythium ultimum, Rhizoctonia solani,* and *Fusarium-Pythium* complex, naturally infested field soil was employed. Only in the case of *Sclerotium rolfsii* was the test organism introduced into the soil to be fumigated.

Failure to control the root knot nematode in field tests is felt to be due to inadequate means of mixing the dust to an effective depth in the soil. This appears to be essential, since the diffusion pattern of *trans*-1,4-dibromobutene-2 in the soil is indicated to be small (2–3 in. radius).

In addition to good disease-control effects when mixed in the soil as a formulated dust in the absence of a seal, it was noted that at fungicidal levels the chemical was not particularly toxic to crop seeds provided water was withheld for 24 hr following treatment and planting. In the case of peas and sugar beets this tolerance was outstanding. Excellent stands were obtained at control dosage levels (*Rhizoctonia* and *Pythium*) when seeds were planted at the same time the chemical was applied.

Results to date indicate, therefore, that *trans*-1,4-dibromobutene-2 may be useful as a solid fungicidal and nematicidal soil fumigant. Since mammalian toxicity tests with *trans*-1,4-dibromobutene-2 have not been completed, final appraisal of the toxicity of the compound cannot be made. However, present data indicate that the material possesses a high degree of mammalian toxicity by inhalation, ingestion, or skin contact. Fortunately, the material is a lachrymator and therefore produces definite warning symptoms.

References

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The Equilibrium between Vitamin B_{12} (Cyanocobalamin) and Cyanide Ion

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Beaven (*1*) has reported recently the reversible formation of a purple complex of vitamin B_{12} (cyanocobalamin) with cyanide ion. We also have observed this reaction, and have studied the equilibrium polarographically. Cyanide ion gives a very well-defined diffusion current at the dropping mercury anode in alkaline solutions (*2*) and thus provides an elegant means for measuring the binding of cyanide by vitamin B_{12}. No free cyanide ion could be detected in solutions of pure cyanocobalamin, and additions of cyanide resulted in further binding to form complexes containing 1 or 2 moles of cyanide in addition to the cyano-group already present in cyanocobalamin.

The procedure was as follows. A standard 0.1 *M* solution of sodium cyanide in 0.1 *M* lithium borate

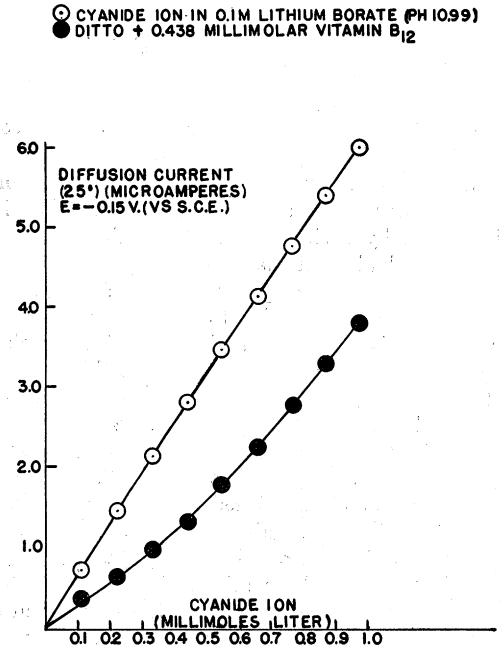

FIG. 1.

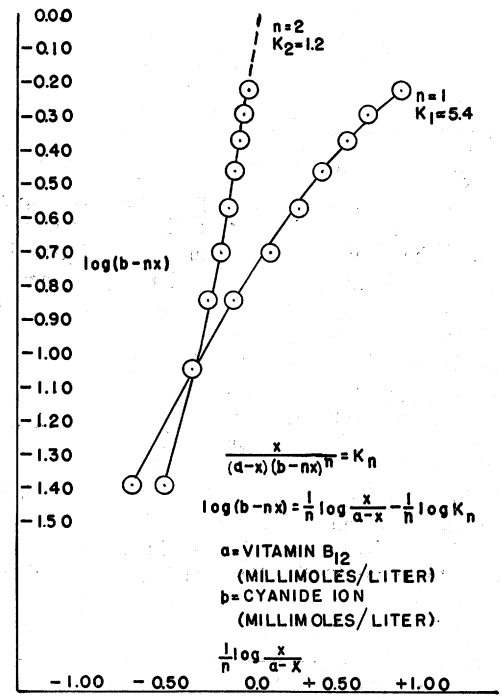

FIG. 2.

buffer, pH 10.99, which was prepared daily from the calculated amount of solid NaCN (purity determined by argentimetric titration), was added in portions from a 0.1-ml Gilmont microburette to an air-free solution of the buffer contained in the polarograph cell at 25°. The polarograph (Leeds & Northrup Electro-Chemograph, Type E) was set at −0.15 v (vs. SCE), and the galvanometer deflection was recorded for each addition. The measurement was then repeated with a similar solution made up to contain also 0.438 mM/l of vitamin B_{12} (a twice-recrystallized sample, purity better than 99%, dry basis) the molecular weight being assumed to be 1,350. A graph of cyanide ion concentration, corrected for hydrolysis, versus diffusion current was prepared, and from this the amount of cyanide ion in equilibrium with vitamin B_{12} and the complex at each level was computed. The results are given in Fig. 1 and Table 1.

TABLE 1

BINDING OF CYANIDE ION BY VITAMIN B_{12}
(All Concentrations in mM/l)

Vitamin B_{12}	Cyanide added	Free cyanide
0.438	0.110	0.041
.438	.219	.090
.437	.328	.145
.436	.436	.199
.436	.545	.269
.435	.653	.345
.434	.762	.428
.433	.869	.515
0.433	0.976	0.598

It was observed that the reaction between vitamin B_{12} and cyanide proceeds at a measurable rate at 25°, 10–15 min being required to establish a steady diffusion current after each addition of cyanide. No such lag was noticed when vitamin B_{12} was absent.

The equilibrium being assumed to be of the type

$$R + n\,CN^- \rightleftarrows R(CN)_n^{n-},$$

the reaction is described by the equation

$$\frac{(x)}{(a-x)\,(b-nx)^n} = K_n,$$

where a represents concentration of vitamin B_{12}, b represents cyanide added, and $b - nx$ free cyanide. In earlier experiments with samples of vitamin B_{12} less pure than that at present employed, a satisfactory constant appeared to be obtained for $n = 2$, but this work indicates that the reaction proceeds in two overlapping stages, wherein first one and finally two cyanide ions are bound. Graphs of the function

$$\log\,(b-nx) = \frac{1}{n}\log\frac{x}{a-x} - \frac{1}{n}\log K_n$$

for $n = 1$ and $n = 2$ are shown in Fig. 2. The curve for $n = 1$ departs from linearity at higher concentrations of cyanide, whereas the reverse is true for the curve of $n = 2$. The limiting values of K_1 and K_2 are estimated to be about 5.4 and 1.2, respectively.

References

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