Trace Analysis of Thiram by Microcoulometry

Thiram, a protective fungicide used in treating plants and seeds, is also used as an animal repellent to prevent damage to newly planted young evergreen seedling trees. This compound has been the cause of sporadic complaints of skin or respiratory tract irritation from exposed field workers. In conducting exposure studies of such workers there is need for analysis of many thiram samples. Existing analytical methodology for that compound is either of low sensitivity or involves lengthy laboratory procedures. Therefore, a rapid analytical method for thiram at the trace (low ppm) level was developed using total oxidation sulfur microcoulometry. The method involves a simple extraction, concentration, and a direct injection. Recovery and linearity are good. An application of the method involved analysis of field respirator pads collected from workers who had planted seedling trees and were therefore exposed to varying amounts of dust from the thiram formulation down to the trace level.

The dithiocarbamate pesticide, thiram [bis(dimethylthiocarbamoyl)disulfide], is used both in agriculture as a fungicide and in reforestation as a repellent to protect newly planted young evergreen seedling trees from damage by wildlife. Workers heavily exposed to this compound occasionally complain of irritation of the eyes, nose, throat, and skin. This created the need for a rapid, sensitive method for the analysis of thiram to evaluate the exposure level of persons who come into contact with this fungicide.

Current methods for the trace determination of thiram generally require either lengthy laboratory procedures (Horwitz, 1975) or expensive instrumentation such as high-pressure liquid chromatography which may not be available to many laboratories. Other methods for thiram analysis (van Hoof and Heyndrickx, 1973; Rappe et al., 1973; and Kettman et al., 1973) do not yield the sensitivity needed in this type of study. Repeated attempts to use gas chromatography according to reported methods (Zweig and Sherma, 1972) or to develop our own GC procedure were unsuccessful. Since many pesticide research and monitoring laboratories have microcoulometers which are used as confirmatory tools in analysis of certain types of pesticides and related substances, a modification of this instrument was used to provide a rapid and sensitive quantitative means for determining levels of thiram ranging down to the trace (ppm) level.

MATERIALS AND METHODS

A Model C-200-AR microcoulometer updated to the C-200-B (1975) electronics standards was used, with bias at 160 mV, gain at 300 in the "Hi" mode, and range ohms at 50 to 100. (All model numbers refer to instruments produced by Dohrmann-Envirotech, Mountain View, Calif.)

A Model S-200 furnace, modified to accept the special oxidation sulfur pyrolysis tube for totals injection, housed in a cast aluminum totals inlet block was used, with argon carrier flow at 26 mL/min and oxygen reactant flow at 160 mL/min. Inlet block temperature was 700 °C, while both the center and outlet furnaces were 800 °C.

A Model T-300-P oxidation sulfur cell was used as the detector, with the inlet arm raised to 50 °C with a heating tape. The reference arm was filled with 20/40 mesh iodine. The cell electrolyte was potassium iodide (0.05%), sodium azide (0.06%), and acetic acid (0.5%) in distilled water. To optimize the cell operation and enhance baseline stability of the recorder, the entire cell unit was enclosed in a standard, lightproof, grounded metal box.

Alpha cellulose pads (25 cm^2), designed for use in determining potential dermal exposure of workers to pesticides (Durham and Wolfe, 1962), were dosed at 0.5 to 20 mg thiram levels to yield from 5 to 200 ng/mL final concentrations for analysis. After the pads were air-dried they were placed in 250-mL Erlenmeyer flasks containing 100 mL of reagent grade toluene and shaken on a Burrell wrist action shaker for 20 min. The solutions were decanted into amber bottles and stored pending analysis. Blank extractions of pads were also carried out to ascertain the extent of impurities, if any, which might interfere with sulfur analysis.

The applicability of the method was demonstrated by analyzing the thiram on pads from special respirators (Durham and Wolfe, 1962) worn by field workers who were exposed to the fungicide while planting treated evergreen tree seedlings. The pads were extracted with reagent grade toluene as described above for dosed pads and, where needed, the final extract was concentrated up to 100:1 with a rotary film evaporator. Extracts from blank pads were also concentrated to determine any interfering sulfur impurities which might have been present.

RESULTS AND DISCUSSION

An injection of up to 3 μL was used with a delivery rate of not more than 1 μL/s. The rate of injection is important to uniform response and must be slow and constant. Slow injection insures complete combustion of solvent and prevents deposition of carbon on the detector cell walls. With good technique, reproducibility was found to be comparable to that obtainable with a series of injections of other pesticides in a gas chromatograph. A workable lower detection limit of 5 ng/μL (5 ppm) was obtained with a range ohms settings of 100 on the microcoulometer, bias at 160 mV, and gain at 300 in the "Hi" mode. These settings allowed a 10% full-scale deflection on the recorder with less than a 1% noise level. The Dohrmann Instrument Company has reported a linear response for between 0.1 to 10 000 ppm for sulfur-containing compounds using an instrument similar to that which was employed in this study (Dohrmann-Envirotech, 1976). The recovery time of the titration cell is very rapid after an injection (2–3 min). This factor contributes greatly to the rapidity of analyses and allows over 150 injections to be made during a normal working day.

Toluene was the solvent of choice because it has favorable combustion properties and sufficient solubility for thiram. Several other solvents were evaluated for these properties including reagent grade, spectral grade, and nanograde types. Of the grades of toluene evaluated, the reagent grade showed the same minimal sulfur response as spectral grade. Both listed sulfur impurities at 0.002% and both gave negligible sulfur response. Because of the significant difference in cost between the spectral and reagent grades, the latter was chosen.

As shown in Table I, recovery of thiram from dosed exposure pads increased from the 0.5 to the 5 mg dosing level and was constant from the 5 to the 20 mg dosing level. Recovery of thiram from exposure pads dosed below 0.5 mg showed detectable but nonquantifiable responses. Low

Table I. Thiram Recovery from Dosed Exposure Pads[a]

Thiram applied to exposure pads, mg	Concn of thiram in final extract, ppm	% recov[b]
0.1	1	c
0.5	5	37.6 ± 3.05
1.0	10	59.6 ± 4.33
2.5	25	79.0 ± 4.18
5.0	50	90.2 ± 4.55
10.0	100	90.2 ± 3.89
20.0	200	89.6 ± 4.16

[a] Details are given in the Experimental Section. [b] Mean ± SD for five replicates. [c] A nonquantifiable response was obtained.

recoveries below the 5-mg dosing level may be due to the saturation of active sites on the alpha cellulose pads with thiram. At the dosing level of 5 mg and above these sites are saturated and recovery is consistent. Below the 5-mg dosing level, thiram may be adsorbing irreversibly on active carbohydrate sites on the alpha cellulose pads. This problem might be circumvented by the use of a more polar solvent, but such solvents do not have optimal combustion characteristics as well as adequate thiram solubility. The curve constructed from these data provides a reliable standard for routine analysis between the 0.5- and 20.0-mg levels.

Results of the analyses of pads from respirators of exposed field workers showed that amounts of thiram found were sufficient to accurately quantitate, with values ranging from 9.3 to 213.8 μg/respirator pad. No interfering sulfur impurities appeared on concentrations of blank extracts.

It should be noted that a limitation of this method is that no chromatographic separation is involved and all sulfur-containing compounds in the sample being analyzed will give a response in the titration cell. Therefore it is specific only for sulfur, not for thiram. This limitation requires careful control of exposure circumstances coupled with analysis of thiram-free control samples, which are collected under nearly identical experimental conditions as the samples of interest. If these requirements are met, one may assume, with a high degree of probability, that thiram is the source of the sulfur response.

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