

Short communication

# New gas chromatographic method for residue determination of dithiopyr in soil, wheat grain and straw

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## Abstract

A gas chromatographic method has been developed for a new pyridine herbicide, dithiopyr, utilising an electron capture detector. The method makes use of a column (10 m×0.534 mm I.D.; 1 μm film thickness) containing HP-1 with nitrogen as a carrier gas at a flow rate of 15 ml min<sup>-1</sup> at temperatures of 190, 210, 270°C for oven, injector port and detector, respectively. Soil, wheat grain and straw samples fortified with dithiopyr were extracted with acetone–0.2 M HCl (95:5) and cleaned up by partitioning with hexane. The technique has a sensitivity of 0.05 μg ml<sup>-1</sup> and the recovery of dithiopyr from soil, wheat grain and straw ranged between 80 and 99%. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Soil; Environmental analysis; Dithiopyr; Pesticides

## 1. Introduction

Dithiopyr [S,S-dimethyl-2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3, 5-pyridinedicar-

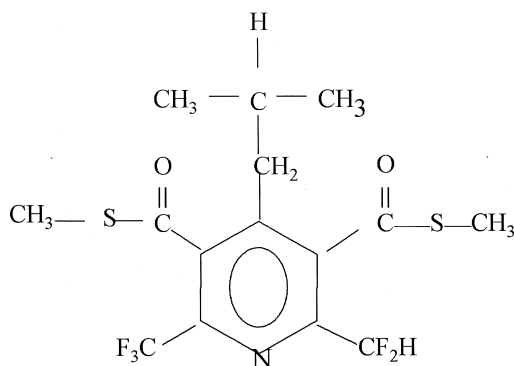


Fig. 1. Dithiopyr.

bothioate], (Fig. 1) is a selective herbicide developed for weed control in turf-grass [2], transplanted rice and other cereals [1,4]. The compound has been reported to have excellent pre- and early post-emergence activity against major narrow leaf and small seeded broad leaf weeds [3,4].

There is not much information available on methods of analysis of dithiopyr in crops. The paper here presents a simple, convenient and sensitive method for determination of dithiopyr in wheat straw, grain and soil by gas chromatography.

## 2. Experimental

### 2.1. Chemicals

Dithiopyr (99.9% purity) was obtained from Rohm and Haas (New Delhi, India). All the solvents

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were distilled prior to use. Anhydrous sodium sulphate was used as a drying agent.

## 2.2. Chromatographic conditions

A Hewlett-Packard GC instrument, Model HP 5890, equipped with a  $^{63}\text{Ni}$  electron-capture detector was used. The stationary phase consisted of a column (10 m $\times$ 0.53 mm I.D.) of HP-1. The operating temperatures for oven, injector and detector were 190, 210 and 270°C, respectively. Nitrogen was used as carrier gas at a flow rate of 15 ml/min. A 3  $\mu\text{l}$  volume of sample was injected on column by auto-injector and chromatograms were visualized on computer. The instrument had a microprocessor controlled data system that allowed the automatic calculation of the detector response in terms of peak area.

## 2.3. Preparation of standards

Dithiopyr (25 mg) was dissolved in hexane in a 25 ml volumetric flask and volume was made up to the mark to give a 1000  $\mu\text{g ml}^{-1}$  stock solution. A 1 ml volume of this stock solution was transferred and diluted up to the mark in a 10 ml volumetric flask using hexane to give a 10  $\mu\text{g ml}^{-1}$  standard solution of dithiopyr. Solutions of different concentrations were prepared by diluting this standard solution. A 3  $\mu\text{l}$  volume of each solution was injected using auto-injector. The method was validated by running solutions of 0.1, 0.2, 0.5, 1 and 2  $\mu\text{g ml}^{-1}$  dithiopyr. Each run was performed in duplicate and the detector response was measured in terms of peak area.

## 2.4. Extraction of dithiopyr

**Soil:** The extraction procedure for dithiopyr was evaluated on a sandy loam soil with a composition of 19.0% clay, 21% silt, 60% sand and 0.35% organic carbon and a pH of 7.2.

A 10 g amount of dried and sieved soil was fortified separately with 10, 20, 30 and 50  $\mu\text{g}$  of dithiopyr. The moist soil (12% field capacity) was extracted with 50 ml of 95% mixture of acetone and 0.2 M HCl by shaking for 30 min on a horizontal shaker and then filtered through a Buchner funnel. The extraction was repeated twice more. All the

filtrates were combined and evaporated to about 5 ml on a rotary evaporator at 35°C.

**Wheat straw and grain:** A 50 g sample of powdered grain and straw were spiked with dithiopyr separately at 0.2, 1 and 2  $\mu\text{g g}^{-1}$  in triplicate. The sample was extracted with 250 ml of a mixture of 95% acetone and 0.2 M HCl using soxhlet for four hours. The extract was evaporated to about 5 ml on the rotary evaporator at 35°C.

## 2.5. Cleanup

The concentrated extract was transferred to a 250 ml separating funnel using 5 ml of 0.02 M NaOH solution. To this were added 1–2 ml of 1 M NaOH solution and 10 ml saturated NaCl solution and partitioned with 50 ml (25+15+10) of hexane. The solvent extract was passed through anhydrous sodium sulphate and evaporated almost to dryness on a rotary evaporator at 35°C. The samples were diluted with hexane and estimated by gas chromatography using peak area.

## 3. Results and discussion

Dithiopyr was resolved as a single peak on a gas chromatograph equipped with a column (10 m $\times$ 0.53 mm I.D.) containing HP-1 and electron-capture detector and had an  $R_t$  of 1.93 min.

The calibration graphs obtained by plotting concentration versus average peak area (each sample injected in duplicate) were linear over the range of 0.1–2  $\mu\text{g ml}^{-1}$ . The sensitivity of the method was 0.05 ng of dithiopyr.

After optimizing the GC conditions, the method was extended to the analysis of soil, straw and grain. There was no interfering peak in any of the matrix blanks, emphasizing satisfactory successful cleanup procedure (Fig. 2) and gave quantitative recoveries ranging between 82.7 and 98.7% for soil, 80.1 and 84% for straw and 82.8 and 89.8% for wheat grains (Table 1). Three-fold injections of 0.02 to 2 ppm of dithiopyr were used to determine the standard deviation. It was found that duplicate injections of each sample were optimum for operating in a 95% confidence interval to obtain the desired precision. Hence accuracy and precision of the GC method for

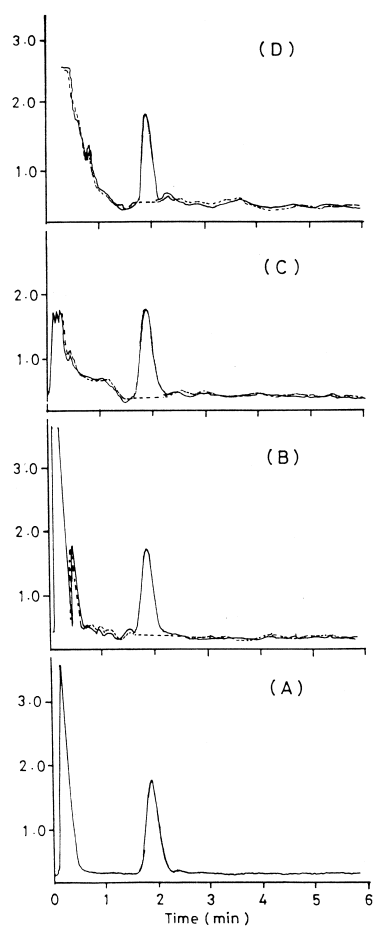


Fig. 2. Gas chromatograms of dithiopyr: (A) standard solution ( $0.1 \mu\text{g ml}^{-1}$ ); (B) soil; (C) straw; (D) grain: (---) blank sample, (—) treated sample.

residue analysis of dithiopyr were adequate for the intended purpose. The limit of detection was also determined. It was found that dithiopyr could be satisfactorily analysed at levels down to 0.05 ppm.

It is concluded that the described GC method is simple and specific for quantitation of dithiopyr from soil and plant material. As the total run time for each

Table 1  
Percentage recovery of fortified samples of dithiopyr from soil, grain and straw

	Treat- ment	Amount added ( $\mu\text{g}$ )	Amount recovered ( $\mu\text{g}$ )	Recovery (%)
Soil	1	10	9.63	96.3
	2	20	19.75	98.7
	3	30	24.81	82.7
	4	50	46.95	93.9
Grain	1	10	8.28	82.8
	2	50	44.5	89.0
	3	100	89.8	89.8
Straw	1	10	8.01	80.1
	2	50	42.00	84.0
	3	100	81.05	81.0

sample was 10 min, this method is suitable for batch analysis.

### Acknowledgements

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### References

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