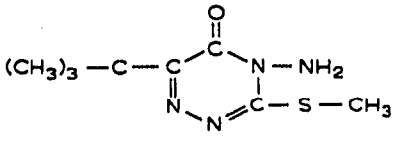
CHROM. 5252

Determination of residues of BAY 94337 (4-amino-3-methylthio-6-*tert.*-butyl-1,2,4-triazin-5-one)

The herbicide BAY 94337 (I) has recently been introduced on a trial basis by the Chemagro Corp., Kansas City, Mo., U.S.A. It is effective at very low doses against broadleaf weeds and grasses[1] and does not seem to accumulate in soil. It is particularly useful in the control of weeds in soybeans, potatoes and sugarcane.



I

A method for the determination of BAY 94337 residues has been reported by STANLEY AND SCHUMANN[2]. The compound was isolated after an elaborate cleanup procedure and was detected by gas chromatography (GC) using an electron capture detection system. It is the purpose of this paper to report a convenient flame photometric detection procedure, which utilizes the fact that the molecule of BAY 94337 contains one sulfur atom. Although the compound responds to electron capture detection, the flame photometric detector, which responds to sulfur in the GC effluent was preferred for the analysis. In contrast to the electron capture detector the flame photometric detector is not easily contaminated by essentially unclean extracts. A time consuming cleaning is therefore avoided. Other advantages are the capability of attenuating its response, specificity and therefore less interference from soil or crop extracts, and a more stable base line.

The sensitivity of analysis by photometric detection is 0.05 p.p.m. The present method has been successfully applied to the determination of BAY 94337 in soil samples fortified with various amounts of the compound.

Materials and procedures

Solvents. All solvents used were of pesticide grade.

Apparatus. A Varian Aerograph Model 204-2B gas chromatograph equipped with a Melpar flame photometric detector (394-mμ interference filter) as described by BRODY AND CHANEY[3] was used. A 5 ft. × 1/8 in. O.D. glass column packed with 10% DC 200 w/v on 100–120 mesh Gas-Chrom Q (Applied Science Laboratories, State College, Pa., U.S.A.) was used for the analysis. A Westronix 1 mV recorder was used to record the chromatogram. The operating conditions are given in Table I.

Procedure. Known concentrations of BAY 94337 were analysed and peak heights recorded in order to prepare a standard curve. The retention time was also determined.

Appropriate amounts of BAY 94337 dissolved in 100 ml of chloroform were added to 100 g of air dried soil in a glass container. The container was then shaken for 20 min using a Fisher-Kendall Mixer with tumbling action.

After the soil/chloroform mixture had been air dried overnight, the soil was extracted with two 100 ml portions of chloroform. The extracts were filtered through

TABLE I

OPERATING CONDITIONS

Carrier gas:	N_2, 50 ml/min
Other gases:	O_2, 20 ml/min
	H_2, 185 ml/min
	Air, 100 ml/min
Injection port:	225°
Column temperature:	200°
Detector (external):	205°
Chart speed:	2/3 in./min

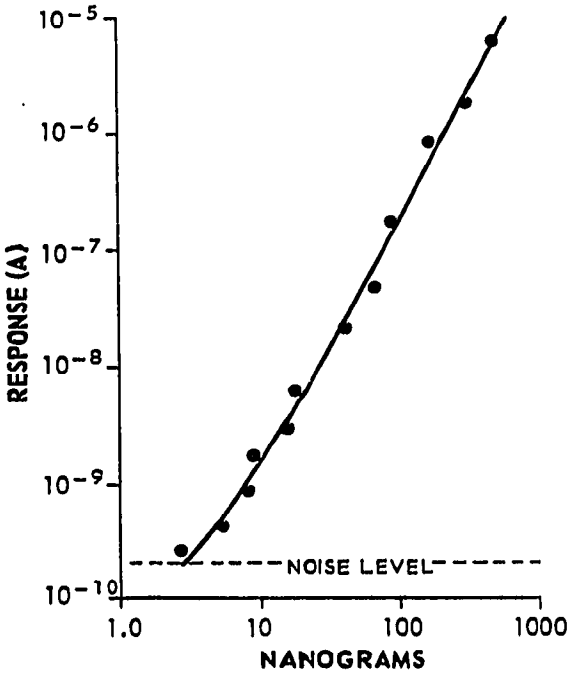


Fig. 1. Standard curve of BAY 94337 with the flame photometric detector (394-mμ filter) on log scale.

TABLE II

GAS CHROMATOGRAPHIC ANALYSIS OF BAY 94337 IN SOIL[a]

Trial	*Compound*	*Added*		*Recovered*	
		p.p.m.	*μg*[b]	*μg*[b]	*%*
1	BAY 94337	0.5	50	48	96
2	BAY 94337	1.0	100	93	93
3	BAY 94337	5.0	500[c]	485[c]	97

[a] Mean of duplicate analyses, 50 mg equivalent of soil injected (2.5 μl) per analysis, except as noted.

[b] Per 100 g of soil.

[c] 10 mg equivalent of soil (2.5 μl) injected.

anhydrous sodium sulfate using a fluted Whatman No. 2 filter paper. The combined filtrates were evaporated to dryness under vacuum in a Buchner flash evaporator at 40° and the residue was taken up in benzene and made up to 5 ml in a volumetric flask. Aliquots of this extract were injected into the gas chromatograph.

Results and discussion

A standard curve for BAY 94337 was prepared (peak height *vs.* concentration) as shown in Fig. 1. Concentrations of unknowns were determined by reference to this curve.

As reported by BRODY AND CHANEY[3] the response to the sulfur flame photometric detector is not linear with concentration; neither was the response of BAY 94337 linear in log–log plot over the three decades of concentration shown in Fig. 1.

The results of analyses of BAY 94337 extracted from soil samples fortified with various levels of the compound are presented in Table II.

The high recovery, 93–97%, of BAY 94337 shows that the method applied can be used for the extraction and determination of this compound in soil.

Typical chromatograms of 25 ng of BAY 94337 are shown in Fig. 2. The retention time for the compound under the conditions stated in Table I was 1.18 min. Chromatogram A shows the standard compound, whereas chromatogram B shows the compound recovered from fortified soil (0.5 p.p.m.). No interference peaks from impurities in the extract were encountered and the base line was stable throughout the analysis.

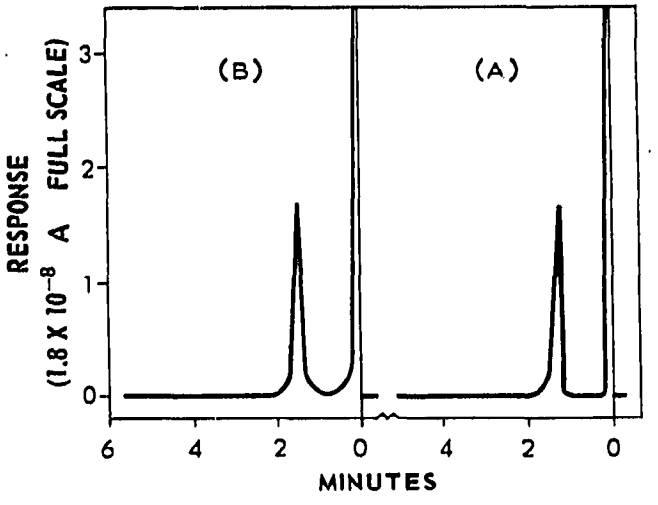


Fig. 2. Chromatogram of BAY 94337. (A) standard, 25 ng injected in 2.5 µl of benzene; (B) extract equivalent to 50 mg of soil fortified with 25 ng of BAY 94337 injected in 2.5 µl of solvent.

It has been shown that the method described can be applied successfully to determine BAY 94337 residues in soil. Tests at present in progress will prove whether the method can also be applied to determine residues of BAY 94337 in plant material.

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Laser pyrolysis of oil shales

In order to evaluate the hydrocarbon content of different oil shales, a rapid laser pyrolysis gas chromatographic technique has been developed. A pulsed ruby laser was used to pyrolyse the samples in a specially designed on-line cell. The results obtained show that the technique is reliable and can provide in a few minutes the total amount of hydrocarbons contained in the shale and additional information not accessible by other techniques presently used.

Pyrolysis units have been used[1] for other purposes and even coupled directly to gas chromatographs[2,3]. Hot wires, heated tubes and cups or heated chambers are often reported[4–6] on these techniques. A high voltage electric discharge pyrolysis has also been tried[7]. A common disadvantage of all these techniques is that they are not very reproducible. A pulsed laser is probably the best available source of energy for analytical pyrolysis. Its output, in conventional mode, can be made stable to within 1% and can be concentrated on any desired area of the sample by simply changing the distance from the focusing lens to the sample.

The laser and pyrolysis cell

We have chosen a water cooled ruby laser for our experiments. The ruby crystal (4 × 9/16 in. of Superior Internal Quality from Union Carbide) is optically pumped by a helical flash lamp surrounded by ceramic reflectors. A quartz roof prism and a sapphire etalon completed the optical cavity. Up to 5,000 J under 5 kV are available from a voltage regulated power supply. Although the ruby could produce 30 J output, energies in the range of 5 to 10 J were found to be sufficient for this investigation. The atmosphere was dry during these experiments; the laser head was maintained at a constant temperature of 16°. The laser shots were separated by exactly 6 min, the time needed to analyze the produced gases. The coupling to the gas chromatograph is such that a new sample was ready by the time the separation was achieved by the column.

The on-line pyrolysis cell required several improvements. The latest model, after three previous prototypes, is shown in the insert of Fig. 1. Cells previously de-