# Confirmation of Atrazine and Fenuron by Alkylation at the ppm Level

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Chemical reactions have been studied extensively as a means of confirming the identity of organochlorine insecticide residues (COCHRANE and CHAU 1971), yet they have found little application for this purpose with triazine or urea herbicides. The formation of silyl derivatives of triazines has been reported by FLINT and AUE (1970), but it gave a mixture of products. Silyl compounds also have a detrimental effect on the response of the alkali flame ionisation detector (AFID) (COWARD and SMITH 1971).

Alkylation with sodium hydride/methyl iodide/dimethyl sulphoxide has been used by GREENHALGH and KOVACICOVA (1974) to derivatise organophosphorus insecticides which possess an NH group. Since nearly all triazine and urea herbicides possess this moiety, the same reaction should be applicable to these compounds. Atrazine and fenuron were used as model compounds to examine the potential of this reaction at the 2 ppm level.

## Experimental

Sodium hydride (10 mg) was washed twice with hexane to remove the oil used as a dispersant. Atrazine or fenuron in hexane (1 ml, conc 2 µg/ml) was added to the sodium hydride in a screwcapped tube, followed by dimethyl sulphoxide (0.1 ml) and methyl iodide (0.1 ml). The tube was stoppered and heated at $50^{\circ}$ for 10 min, then cooled before water (1 ml) was added to destroy excess sodium hydride. The hexane layer was removed, and the solution extracted twice with hexane (0.5 ml). The extracts were combined, taken down to 1 ml and analyzed by GC.

A Pye model 134 gas chromatograph was used equipped with an AFID detector (RbCl annulus). A 5' x 1/4" glass column was packed with 100/120 mesh Gas Chrom Q coated with 4% SE-30/6%-QF-1. The column flow was maintained at 40 ml/min nitrogen and the temperature at $204^{\circ}$.

## Results and Discussion

A gas chromatogram of atrazine (2 µg/ml) before and after alkylation with sodium hydride/methyl iodide/dimethyl sulphozide is shown in Fig. 1A and B. A mass spectrum of the product (rel. RT 1.11) gave a molecular ion m/e 243, indicating both the NH ethyl and NH isopropyl groups had been alkylated to give dimethyl atrazine. The yield was 86%, assuming the AFID response to be the same as for atrazine.

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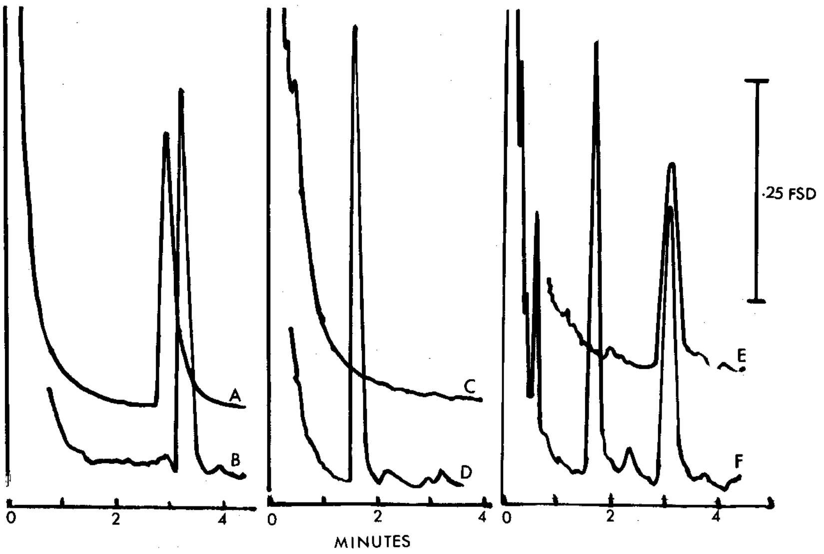

Fig. 1. Gas chromatograms of (A) atrazine 12 ng, (B) alkylated atrazine; (C) fenuron 25 ng, (D) alkylated fenuron; (E) crude soil extract, (F) fenuron fortified extract alkylated.

With the GC conditions employed, fenuron could not be chromatographed, however, after alkylation (2 µg/ml level) it was readily detected, Fig. 1 C and D. A mass spectrum of the product showed a parent ion m/e 178, corresponding to methyl fenuron. A crude methanol extract of an organic soil (10 g) was fortified with fenuron (2 ppm) and alkylated by the above procedure. A gas chromatogram of the hexane extract of the alkylated material indicated the presence of fenuron, in addition to an unknown compound present in the original crude extract, Fig. 1 E and F.

Alkylation with sodium hydride/methyl iodide/dimethyl sulphoxide gives derivates of atrazine and fenuron which can be used to confirm their identity at the ppm level. The method should be applicable to other triazine and urea herbicides.

## References

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