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## Note

# Electron-capture gas chromatographic determination of residues of anthraquinone bird repellent

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Anthraquinone has long been used as a bird repellent[1], for which purpose it is formulated as a seed dressing, 2.5% (w.p.), or is used in admixture with other seed protectants[1,2]. The analysis of the formulation is carried out by gravimetry[1].

Even though the product has a very low toxicity[1], a method is needed for the determination of its residues in soil, seeds and crops, and various procedures have been described for the analysis of 9,10-anthraquinone and its analogues and derivatives. Polarographic[3–7] and titrimetric[8,9] methods have been reported for technical products and mixtures; colorimetric[10] and fluorimetric[11] methods were used for toxicological studies, which need higher sensitivities. Anthraquinone has also been detected by "spot test" analysis[12] and by thermochromic analysis[13]. However, the more frequently used procedures are based on thin-layer chromatography (TLC), followed by different methods of quantitative or semi-quantitative evaluation[14–23]. In particular, one paper[23] reported a toxicological study on anthraquinone specifically used as a bird repellent.

On the other hand, the literature on the gas–liquid chromatographic (GLC) analysis of 9,10-anthraquinone is very scarce. Kogan *et al.*[24] used a stainless-steel column packed with 8% PEGA and a flame-ionization detector for the analysis of technical anthraquinone; Allebone *et al.*[25] used GLC and TLC, as well as mass, UV and IR spectrometry to detect and identify 9,10-anthraquinone in the cuticular wax of the grass *Lolium perenne*. The columns used by Allebone *et al.*[25] were 5% Apiezon L and 3% OV-17 with a flame-ionization detector.

The aim of this work was to develop a very sensitive method to detect and evaluate quantitatively the residues of 9,10-anthraquinone bird repellent in seeds, crops and soil.

Considering the highly conjugated nature of the 9,10-anthraquinone molecule, a good electron affinity was assumed. Moreover, anthraquinone is characterized by a high triplet-energy state, showing a photosensitizing broad spectrum of activity, also towards other pesticides[26].

Therefore, a GLC procedure with an electron-capture detector (ECD) was tried and satisfactory results for sensitivity and specificity were obtained.

## EXPERIMENTAL

### *Extraction and clean-up*

The sample (50 g) is macerated with 150 ml of benzene in an Omni-Mixer apparatus (Sorvall Inc., Norwalk, Conn., U.S.A.), and the slurry is filtered, under suction, through a layer of Filter-Cel and sufficient anhydrous sodium sulphate. The clear filtrate is evaporated to 1–2 ml in a rotary evaporator (Rotavapor E, W. Büchi, Flawil, Switzerland). A chromatographic column (30 × 2.5 cm I.D.) is filled to a height of 10 cm with activated (130° overnight) silica gel (particle size 0.05–0.20 mm for chromatography, Carlo Erba, Milan, Italy) and pre-wetted with light petroleum (b.p. 30–50°), and the extract is transferred quantitatively with *n*-hexane into the column. The column is then eluted with, in order: 100 ml of light petroleum (b.p. 30–50°) and 100 ml of light petroleum–diethyl ether (94:6), both eluates being discarded; and 150 ml of light petroleum–diethyl ether (85:15), the eluate being collected in a 300-ml flask. This eluate is concentrated to suitable volume and analyzed by GLC–ECD.

### *Gas chromatography*

A Varian Aerograph 1440 GLC apparatus, equipped with a tritium foil ECD, a Speedomax W (Leeds & Northrup, North Wales, Pa., U.S.A.) 1-mV full-scale range recorder and Hamilton 701N microsyringes were used.

Various columns were tried and a Pyrex glass column (210 × 0.3 cm I.D.), packed with 3% OV-17 + OV-210 (1:1) on 100–120-mesh Gas-Chrom Q, was chosen. The carrier gas (nitrogen) flow-rate was 60 ml/min and the injection block, detector and column oven temperatures were 210°, 210° and 185°, respectively. Under these conditions, 9,10-anthraquinone has a retention time of 6 min, which permits the prior elution of several peaks due to extraneous substances, which could interfere in the analysis (Fig. 1).

Another column can be used for the determination of anthraquinone, operating under the same conditions, but with an oven temperature of 195°, namely the 200-cm 10% DC-200 on 80–100 mesh Gas-Chrom Q column, which is the classical column used for pesticide residue analysis[27]. Quantitative determinations are carried out by alternate injections of the sample extract and of a benzene solution containing 1 $\mu$g/ml of pure 9,10-anthraquinone.

## RESULTS AND DISCUSSION

The procedure was applied to samples of wheat and maize seeds, fresh peas and agricultural soil. Recoveries were 94–106% in the range 0.5–0.05 ppm. The maximum sensitivity was about 0.05 ppm.

The linear dynamic range was measured for both columns, the 3% OV-17 + OV-210 column operating at 185° and the 10% DC-200 column at 195°.

The response to 9,10-anthraquinone is linear in the range 0.1–15.0 ng, as shown in Fig. 2, and is the same for the two different columns. The sensitivity is also the same for the two columns and the minimum detectable amount is about 0.1 ng. These performances were obtained with a standing current of $0.65 \cdot 10^{-8}$ A, corresponding to about 22% deflection of the recorder, at an attenuator setting of $32 \cdot 10^{-9}$.

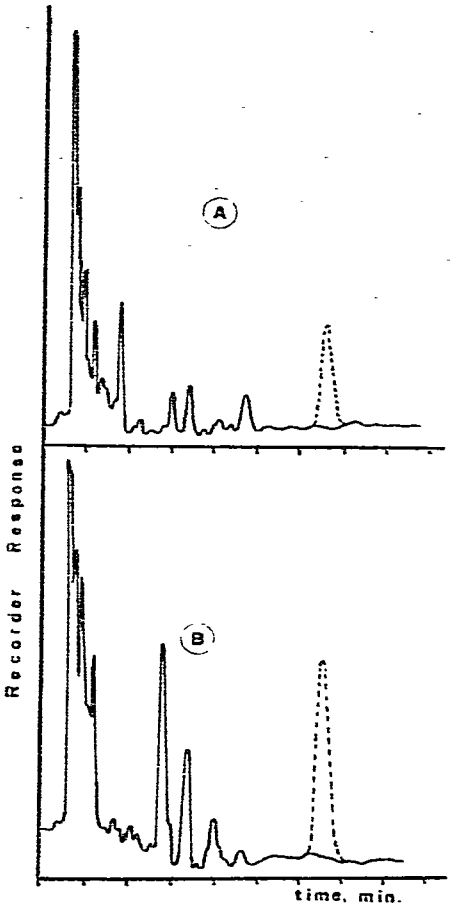


Fig. 1. Separation of anthraquinone on a 3% OV-17 + OV-210 (1:1, w/w) column. A, 5 $\mu$l of pea extract added with 0.14 ppm of 9,10-anthraquinone; B, 2 $\mu$l of wheat seed extract added with 0.58 ppm of 9,10-anthraquinone. Similar behaviour was shown by maize seeds and agricultural soil extracts.

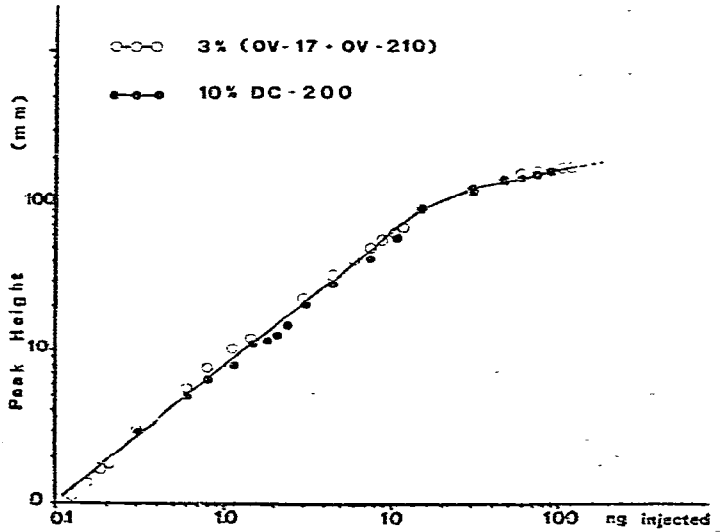


Fig. 2. Typical linearity curve for 9,10-anthraquinone, operating on 3% OV-17 + OV-210 and 10% DC-200 columns at 185° and 195°, respectively.

A very recent paper[28], published after the first submission of this paper, reported the GLC–ECD determination of anthraquinone derived from oxidation of amitriptyline; temperature dependence of the ECD response of anthraquinone was demonstrated and a minimum detectable amount of 40 pg was achieved.

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