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PRU 1497-M

HPLC METHOD FOR THE ANALYSIS OF BROMOXYNIL AND IOXYNIL IN WATER

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May 1987

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SUMMARY

An HPLC method is described for the determination of bromoxynil and ioxynil in water. If a clean-up stage is included a detection limit of about 0.1 µg l^{-1} can be obtained. Without the clean-up the detection limit is about 1 µg l^{-1}.

CONTENTS

1. OUTLINE OF THE METHOD

Water samples (100 ml) are extracted using C_{18} Sep-pak cartridges. Separation and quantification is carried out using reversed-phase HPLC with UV and electrochemical detection. The method was based on that published by Brown et al 1984.

2. EQUIPMENT

HPLC solvent delivery system; UV detector capable of monitoring at 280 nm, electrochemical detector capable of monitoring at a potential of + 1.15 v.

3. HPLC ELUTION AND DETECTION

Bromoxynil and ioxynil are eluted using identical HPLC elution conditions;

Column: Reversed-phase (C_{18}, 25 cm x 4.6 mm i.d.)

Eluent: Methanol-water (1:1) with the addition of sodium acetate (8.2 g per litre of eluent) and formic acid (0.3% v/v).

Flow rate: 1 ml min^{-1}

Detection: UV absorption at 280 nm.
Electrochemical at a potential of + 1.15 v.

Under these conditions, bromoxynil is eluted at a retention time of about 10 min and ioxynil at a retention time of about 15 min. With a UV detector sensitivity of 0.002 aufs and an electrochemical detector sensitivity of 100 nA, the following instrumental detection limits (ng injected on column) are obtained;

	UV	Electrochemical
Bromoxynil	0.5	0.03
Ioxynil	0.5	0.05

4. EXTRACTION

Details of two methods of extraction are provided, and the method chosen depends on the limit of detection required. For samples which require a detection limit of <1 µg l^{-1} a clean-up stage has to be included to remove interfering compounds from the extract.

Inclusion of a clean-up stage results in some loss of both compounds. However, this stage can be left out for samples which require a detection limit of >1 µg l^{-1}.

4.1 Method for a detection limit <1 µg l^{-1}

Water samples (100 ml) are adjusted to pH 10 with 2 M sodium hydroxide and then eluted through a clean C_{18} Sep-pak cartridge (Note 1). The eluate is collected, adjusted to pH 2 with concentrated hydrochloric acid, and eluted to waste through a second clean C_{18} Sep-pak cartridge. Elute the cartridge with methanol (2 ml), collect the eluate and concentrate to the required volume under a stream of nitrogen.

4.2 Method for a detection limit >1 µg l^{-1}

Water samples (100 ml) are adjusted to pH 2 with concentrated hydrochloric acid and eluted through a clean C_{18} Sep-pak cartridge. Elute the cartridge with methanol (2 ml), collect the eluate and concentrate to the required volume under a stream of nitrogen.

5. PERFORMANCE CHARACTERISTICS

The method has not been fully characterised but a series of spiking experiments have been carried out using water from a lowland river. Results for the method with clean-up are provided in Table 1 and without clean-up in Table 2.

Table 1

Concentration ($\mu g\ l^{-1}$)	Recovery (%)*	
	Bromoxynil	Ioxynil
0.1	65, 56, 58	41, 41, 45
1.0	70, 61, 67, 59, 72, 60	64, 46, 40, 36, 47, 45
10.0	82, 63, 75	64, 43, 55
50.0	69, 75	51, 44

* More than one figure refers to results from repeat determinations

Table 2

Concentration ($\mu g\ l^{-1}$)	Recovery (%)*	
	Bromoxynil	Ioxynil
1.0	75, 69	90, 85
10.0	88, 86	76, 84

* Figures refer to repeat determinations

6. DISCUSSION

In order to obtain a detection limit below 0.1 $\mu g\ l^{-1}$ it is necessary to use an electrochemical detector, which is more sensitive to these compounds than a UV detector (Section 3). However, at this low level there is interference from other compounds present in extracts from river water samples. Interfering compounds can be removed using the clean-up procedure described in Section 4.1, but this does lead to poorer recovery, particularly for ioxynil. For monitoring samples for which a detection limit of >1 $\mu g\ l^{-1}$ is satisfactory, then the clean-up stage can be omitted.

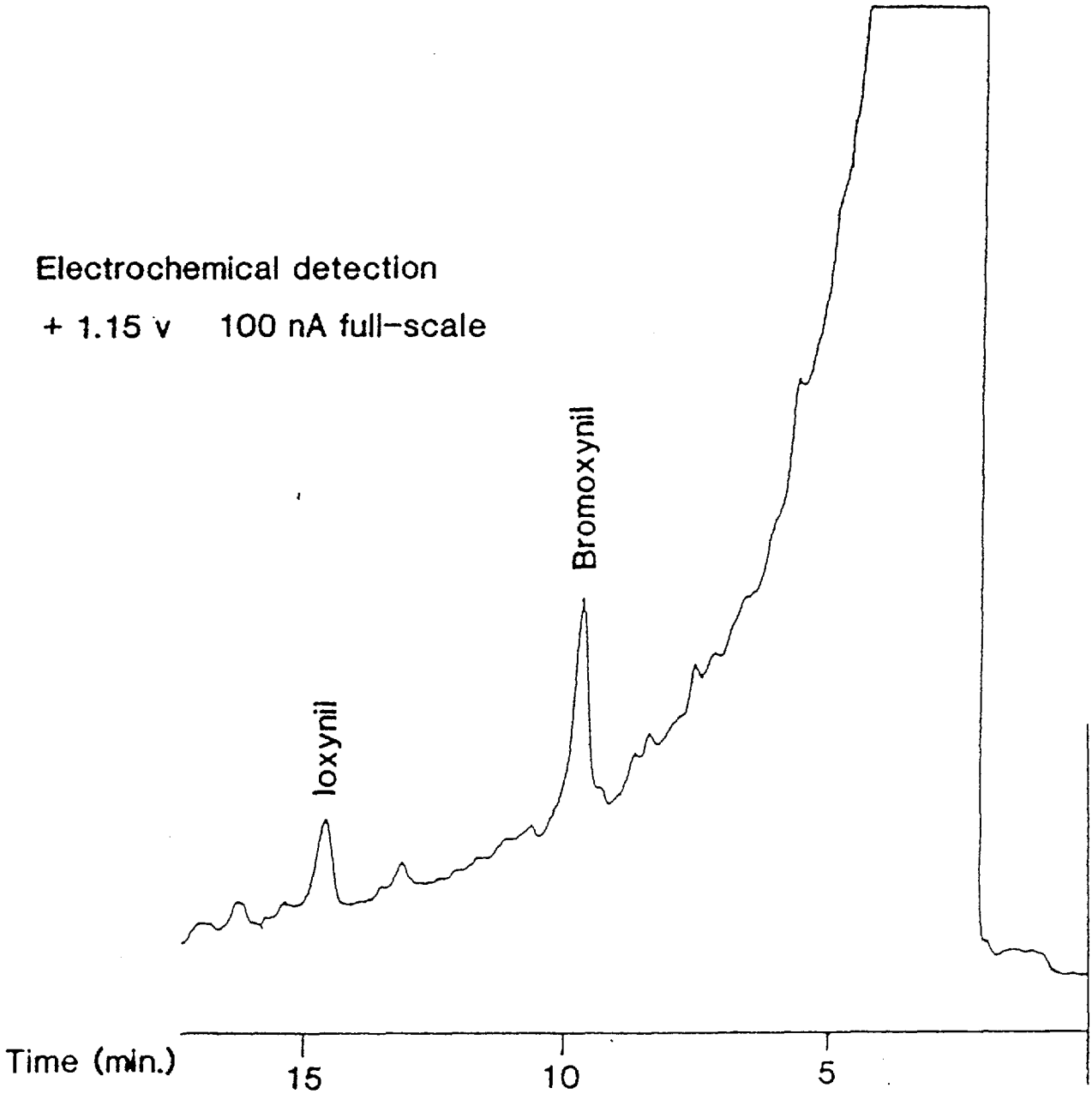
The specificity of the method is considerably enhanced by using UV and electrochemical detectors in series, however if unambiguous confirmation of the result is required, particularly at concentrations <1 μg l^{-1}, then application of another technique (eg mass spectrometry) is necessary.

The HPLC separation of a spiked river water (0.1 μg l^{-1}) extract is shown in the Figure.

Note 1 Sep-pak cartridge are available from Millipore (UK) Ltd. Cartridges should be cleaned before use as follows; elute the cartridge successively with methanol (20 ml), dichloromethane (20 ml), methanol (20 ml) and deionised-distilled water (2 ml).

REFERENCE

BROWN D F, McDONOUGH L M, McCOOL D K and PAPENDICK R I (1984) HPLC determination of bromoxynil octanoate and metribuzin in runoff water from wheat fields. Journal of Agric Food Chem, 32(3) 195-200.



HPLC separation of a spiked river water (0.1 $\mu g l^{-1}$) extract