

## DETERMINATION OF PHENMEDIPHAM AND DESMEDIPHAM IN A COMMERCIAL HERBICIDE BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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*Betanal AM-11 is the herbicide that is using to control one-year old weeds with wide leafs in sugar beet fields. Active ingredients of the herbicide are phenmedipham and desmedipham. Commercial emulsifiable concentrate (EC) contains 80 g/L  $\pm$  10% of each active compound. We applied high performance liquid chromatography (HPLC) with diode array detector (DAD) at 254 nm for the determination of phenmedipham and desmedipham in commercial samples of Betanal AM-11. This method involves reversed-phase separation of the components on C-18 bonded silica with methanol-water (51+49, v/v) as the eluent. The procedure was highly selective and reproducible and can be successfully used in determining contents of phenmedipham and desmedipham on micro and macro levels.*

KEYWORDS: Phenmedipham; desmedipham; HPLC-DAD; determination

### INTRODUCTION

Phenmedipham (PMP) and desmedipham (DMP) are widely used as selective herbicides for broad leaf weed control in beet crops, especially in sugar beet crops. Crops are treated at temperatures bellow 20°C, when beet has 2 to 3 straight leafs and weeds has 1 to 3 leafs. The Herbicide Betanal AM-11, with active ingredients phenmedipham and desmedipham, is produced in Serbia and Montenegro. Production is discontinuous. Commercial emulsifiable concentrate (EC) contains 80 g/L  $\pm$  10% of each active compound.

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Phenmedipham has been classified in the so-called black list published in the 76/464/0EEC Directive (1).

Phenylcarbamate herbicides are generally determined by gas chromatography (GC) with electron-capture detection (ECD), flame ionization detection (FID) and mass spectrometry detection (MS) or by high-performance liquid chromatography (HPLC) with ultraviolet (UV), MS and other detection (see, e.g. 1-3). Schering Analytix (4) used the HPLC method with spectrometrical detection for the determination of phenmedipham and desmedipham in Betanal AM-11.

Hidalgo et al. (1) described the sensitive determination of phenylcarbamate herbicides (desmedipham, phenmedipham, etc.) in environmental waters and Junker-Bucheit and Witzembacher (5) in drinking water by reversed-phase liquid chromatography with diode array detection (DAD).

In this paper we report a reversed-phase (RP) HPLC-DAD procedure for quantitative determination of phenmedipham and desmedipham in commercial herbicide Betanal AM-11.

## EXPERIMENTAL

### *Chemicals*

Phenmedipham (purity 99.8%) and desmedipham (purity 99.6%) were obtained from Riedel de Haën (Fluka Chemie, Buchs, Switzerland). A standard solution was prepared by dissolving 10 mg of each herbicide in 10 mL of methanol acidified with acetic acid (3 mL of concentrated acetic acid added to 1 L of methanol) and diluted to 100 mL with eluent.

Methanol was HPLC grade from Riedel de Haën (Fluka Chemie, Buchs, Switzerland). Acetic acid was of analytical-reagent grade (Zorka, Šabac, Serbia and Montenegro). HPLC-grade water was obtained by deionisation of distilled water.

### *Sample preparation*

An amount of 70-80 mg ( $\pm 0.1$  mg) Betanal AM-11 samples were dissolved in 5 mL of methanol acidified with acetic acid and diluted to 50 mL with eluent. Samples of the liquid concentrate Betanal AM-11, marked 1-18, have been taken before packing of every batch of prepartate, during two months long production.

### *HPLC apparatus*

A Model 1100 liquid chromatograph (Hewlett-Packard) equipped with a septum programmable injector, binary pump, diode array detector and a Hypersil ODS column (200  $\times$  2.1 mm I.D., particle size 5  $\mu$ m) was used. The mobile phase was methanol – water (51:49, v/v) at a flow-rate of 0.4 mL/min. All experiments were carried out at 20°C. Herbicides were monitored at 254 nm. Autointegration of the peaks was used in the relationship with the baseline. The percent of active ingredient (*A.I.*, %) of the herbicide in Betanal samples, i.e. the phenmedipham and the desmedipham, were obtained by comparing the areas of the peaks of the samples and of the standard solution. The content (*C*) of the herbicides (g/L) was calculated using the equation:

$$C = A.I. \times d \times 10 [\text{g/L}]$$

where  $d$  is the density, g/mL (6) and  $A.I.$  is active ingredient, %.

#### *Physico-chemical parameters of the products*

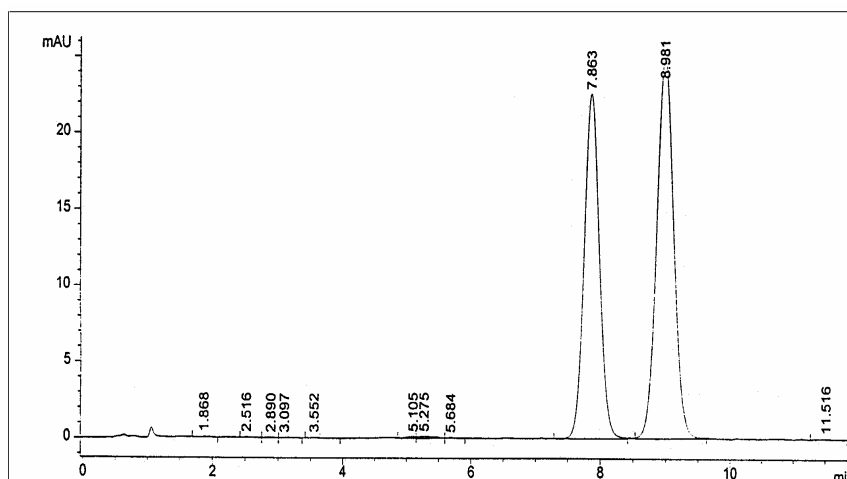
pH value and density of emulsifiable concentrates of Betanal AM-11 were determined according to the methods described in reference (6).

### RESULTS AND DISCUSSION

The commercial herbicide Betanal AM-11 was obtained by batch production. The active ingredients are 8% PMP and 8% DMP with 10% allowed deviation. Herbicide quality mark is declared with content of active compound and its physical characteristics. To prevent environmental pollution and control manufacturing process efficiency, the product quality is continuously controlled.

In our laboratory, a modification of Analytical Method No. 0654-LC-04 (4) was studied to determine PMP and DMP in commercial products of the herbicide Betanal AM-11. The method was modified because operating conditions (detector, flow rate, length, internal diameter, adsorbent and particle size of column) were different.

Chromatographic separation was performed on a C-18 column using DAD at 254 nm. In all the experiments the injection volumes were 2  $\mu\text{L}$ . Good resolution of PMP and DMP with suitable peak shape was obtained with the eluent methanol-water (51:49, v/v). Figure 1 shows typical chromatographic separation of DMP (retention time 7.863 minutes) and PMP (retention time 8.981 minutes) in a standard mixture solution.



**Fig. 1.** Direct LC-DAD chromatogram ( $\lambda=254$  nm) of a standard mixture solution DMP-desmedipham ( $t_R=7.863$  min) PMP-phenmedipham ( $t_R=8.981$  min)

The relative standard deviation of retention times for both components were about 0.1% (n=8). The differences of the individual areas were less than 1% from their mean value.

Under chromatographic conditions selected, the limit of detection (signal to noise ratio = 10) was 2.9 µg/ml for DMP and 2.7 µg/ml for PMP.

Table 1 and Fig. 2 show the results of the analysis of commercial herbicide, i.e. the content of PMP and DMP in 18 samples of Betanal AM-11. In Table 1 are shown also some other physico-chemical parameters of the samples (6).

**Table 1.** pH values, density and content of desmedipham and phenmedipham in herbicide samples

Sample	pH	d <sup>20</sup> (g/mL)	Desmedipham		Phenmedipham	
			A.I.* (%)	C** (g/L)	A.I.* (%)	C** (g/L)
1	3.49	0.9864	7.50	73.98	7.69	75.85
2	3.53	0.9876	7.66	75.65	7.80	77.03
3	4.16	0.9856	7.86	77.47	7.72	76.89
4	4.18	0.9864	7.98	78.71	7.85	77.43
5	4.09	0.9868	7.83	77.27	7.76	76.57
6	4.08	0.9866	7.82	77.15	7.69	75.87
7	4.15	0.9895	7.94	78.57	7.62	75.39
8	4.18	0.9890	8.35	82.58	7.71	76.25
9	4.17	0.9866	8.38	82.67	7.98	78.73
10	4.15	0.9861	8.03	79.18	7.89	77.80
11	4.08	0.9856	8.03	79.14	7.92	78.06
12	4.11	0.9856	8.12	80.03	7.91	77.96
13	4.09	0.9853	8.15	80.30	7.96	78.43
14	4.05	0.9853	8.48	83.55	8.26	81.38
15	4.05	0.9859	8.15	80.35	8.05	79.36
16	4.04	0.9861	8.23	81.15	8.06	79.47
17	4.03	0.9847	8.08	79.56	8.05	79.26
18	4.06	0.9852	8.44	83.15	8.32	81.96

\*Active ingredient; \*\*Content

The parameters of in-process control of pH and density of emulsifiable concentrates were satisfied (Table 1): pH 3.49-4.18 (limit 3-5); density 0.9847-0.9895 g/mL (limit 0.98-0.99 g/mL) (4).

The content of active ingredients, i.e. DMP and PMP, in emulsifiable concentrates were 8±0.21% and 8±0.17% respectively (Table 1, Fig. 2). The relative standard deviation of retention times varied from 0.51 to 0.27%, respectively, for DMP and PMP which are the compounds to be eluted last from the HPLC column. The differences of individual areas were also less than 1%. The detection limits obtained for each active ingredient were lower than 3 µg/mL.

This selective and reproductive RP-HPLC (DAD) procedure is a suitable method for the analysis of PMP and DMP during the production of herbicide Betanal AM-11, i.e. for the analysis of these active ingredients at macro and micro levels.

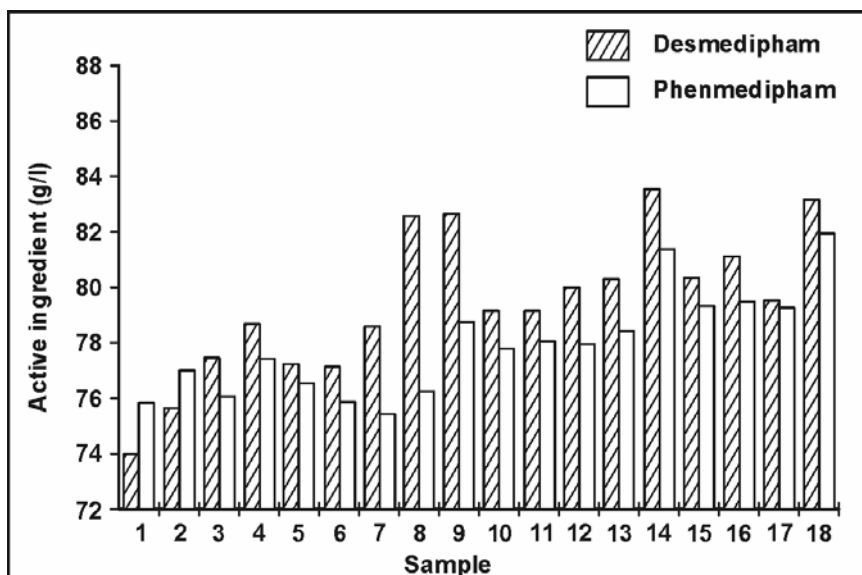


Fig. 2. Content of desmedipham and phenmedipham in herbicide samples

### CONCLUSION

The active ingredients of the commercial herbicide Betanal AM-11, desmedipham and phenmedipham, were separated using RP-HPLC with eluent methanol-water (51:49, v/v) and detected by DAD. The relative standard deviations of retention times and individual areas were less than 1%. The detection limits below 3 µg/mL were obtained for each active ingredient.

### ACKNOWLEDGMENTS

This work was supported by the Ministry of Science, Technologies and Development of the Republic of Serbia (Project 1775, 2002-2004).

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### **ОДРЕЂИВАЊЕ ФЕНМЕДИФАМА И ДЕСМЕДИФАМА У КОМЕРЦИЈАЛНОМ ХЕРБИЦИДУ ТЕЧНОМ ХРОМАТОГРАФИЈОМ ПОД ВИСОКИМ ПРИТИСКОМ**

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Бетанал АМ-11 је хербицид који се користи за сузбијање једногодишњих широколисних корова на пољима са шећерном репом. Активни састојци хербицида су фенмедифам и десмедифам. Комерцијални концентрат за емулзију (ЕС) садржи  $80 \text{ g/l} \pm 10\%$  сваке активне компоненте. За одређивање фенмедифама и десмедифама у комерцијалним узорцима Бетанала АМ-11 је примењена течна хроматографија под високим притиском, DAD детектор и таласна дужина од 254 nm. Метод је обухватио раздвајање компонента на обрнутим фазама са колоном С-18 и елуентом метанол-вода (51+49, v/v). Поступак је веома селективан и репродуктиван и може се користити за одређивање макро- и микро количина фенмедифама и десмедифама.

Received 8 April 2004  
Accepted 17 June 2004