

## QUALITY CONTROL OF PESTICIDES, CONTAINING MULTIPLE ACTIVE INGREDIENTS

Grynko A., Mykhaylov V., Kuznetsova E., Aleynov P.

### Introduction

Pesticides of different chemical classes are widely used in agriculture and public health worldwide. In order to increase the biological effectiveness, reduce pesticide load on the human and environment manufacturers design pesticide formulations with several active substances of different chemical classes with different mechanisms of action and direction. Figure 1 presents the trend in the number of registered in Ukraine formulations with multiple active ingredients.

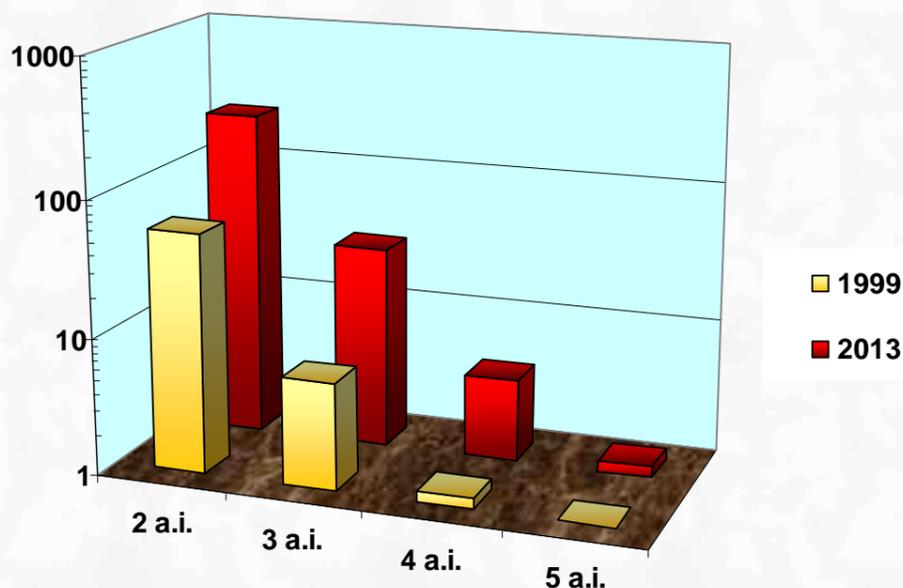


Figure 1. Number of pesticides with multiple active ingredients registered in Ukraine

As we can see, the amount of pesticides with multiple a.i. increased, which complicates the task of quality control. Determination of a.i. conducted according to official CIPAC or AOAC methods. This chromatographic conditions often can not be used when we analyzed formulation with multiple active ingredients.

Therefore, the development and single-laboratory validation of new multi-pesticide method for analysis of pesticide formulations is very important. The concept for developing these new methods is based on experience gained with multi-residue analysis of pesticides. A multi-pesticide method determines the active ingredient content in pesticide formulation using the same sample preparation, chromatographic column and elution system. If available, sample must be prepared and extracted according to a collaboratively tested CIPAC or AOAC method.

Now in Ukraine SC formulation, containing prochloraz, cyproconazole, fludioxonil is registered. There are two methods: reverse phase HPLC method (CIPAC/407) for the determination of prochloraz in TC and EC formulation and reverse phase HPLC method (CIPAC/600) for the determination of cyproconazole in TC, EC and WG formulations. Methods are intended for separate determination of the analysed substances in different chromatographic conditions. CIPAC method for determination of fludioxonil in formulations is lack. Development of the method of simultaneous determination of a.i. in SC formulation was the purpose of work.

### Experimental

#### Working Solutions

The analytical standards of prochloraz, cyproconazole, fludioxonil and internal standard - benzanilide with known purity were used for preparation of stock and working standard solutions.

Stock solutions of a.i. and internal standard (i.s.) were prepared at concentration of about 1.0 mg/ml. Three mixed working solutions were prepared by three independent dilutions at concentrations of about 0.5, 1.0, 1.5 times of the nominal concentrations of active ingredients in the formulated product, respectively, and for each solution was added the same amount of benzanilide.

#### Sample preparation

Five different batches of commercially available SC formulations were used. Sample solutions were prepared so that the final concentration fell within the concentration range of the working solutions.

#### GC system and conditions

The gas chromatographic system used was a ThermoFinnigan Trace GC Ultra with FID detector. The column with low polarity was used: HP-5 (30 m \*0,32 mm\* 0,25 mkm)

Operating conditions: flow rate through column: 1,5 ml/min, split ratio set at 5. Temperature program was the following: the oven temperature held at 80 °C for 1 min, then heated to 200°C at heating rate 30°C/min, kept 2 min, then heated to 280°C at heating rate 15°C/min, kept 3 min.

### Results and discussion

Typical chromatograms of standard and sample solutions are presented on Figure 2,3.

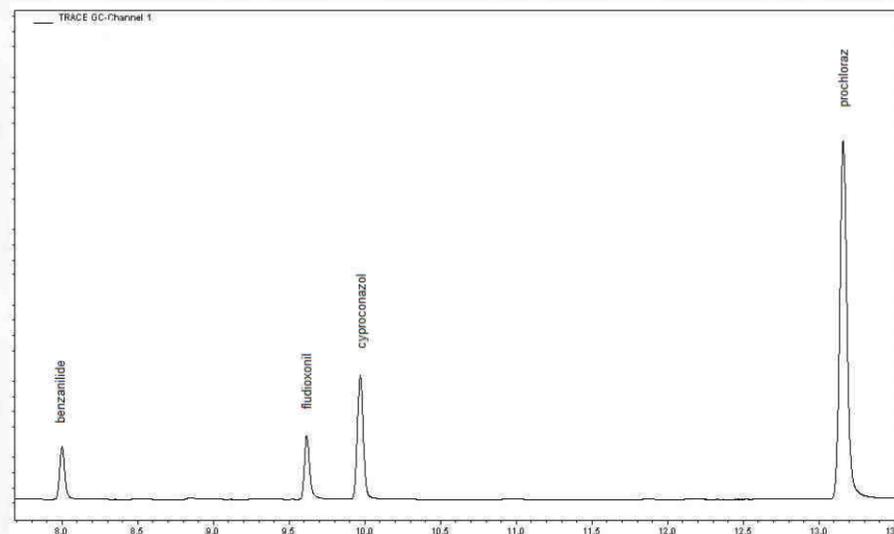


Figure 2. Typical chromatograms of standard solution

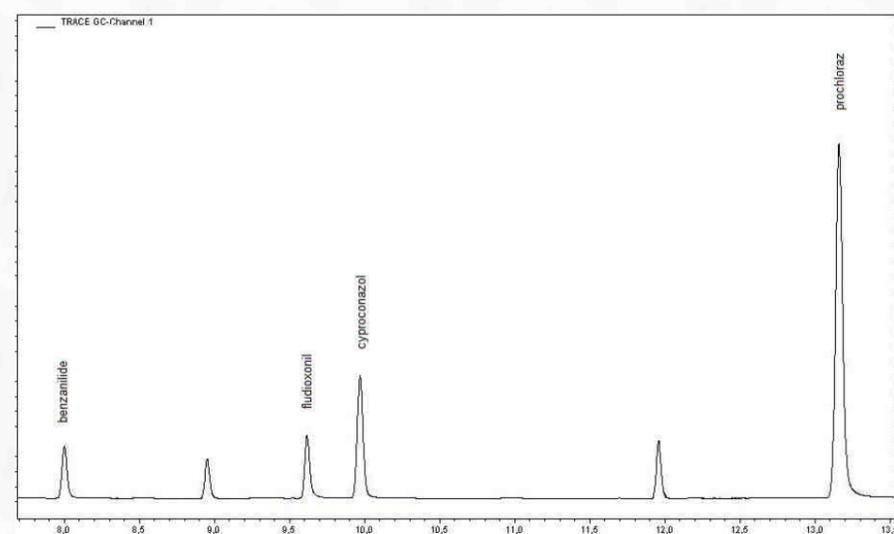


Figure 3. Typical chromatograms of sample solution

Summary information of analytical performance parameters of the method presented in Table 1.

Specificity	Interference from co-fomulants	No interfering peaks were detected from co-formulants in blank chromatogram in the region of fludioxonil, cyproconazol, prochloraz and benzanilide peaks.		
	Peak identity	The retention times of active substances and reference substances are identical.		
Linearity	Correlation coefficient	0,998	0,997	0,997
	Regression equation	y=0,178x+0,004	y=1,738x+0,106	y=1,277x+0,297
Precision (5 samples from one batch; single injection) RSD, %		Acceptable according Horwitz equation; no outliers		
		0,56	0,85	0,76
Accuracy (5 samples of laboratory-prepared synthetic formulation)	Recovery, %	100,3	99,8	100,5
	RSD, %	1,28	1,35	1,16

### Conclusions

The proposed analytical method allows determination of three active ingredients in SC formulation simultaneously.

The use of programmable capillary gas chromatography allows a good separation of the target molecules from possible interfering compounds.

For each analyte, the calibration curves and the corresponding performance parameters (linearity, repeatability) were calculated and gave good results.