

## Aminopyralid, Clopyralid and Picloram in cereals extracts using AFFINIMIP® SPE Picolinic Herbicides

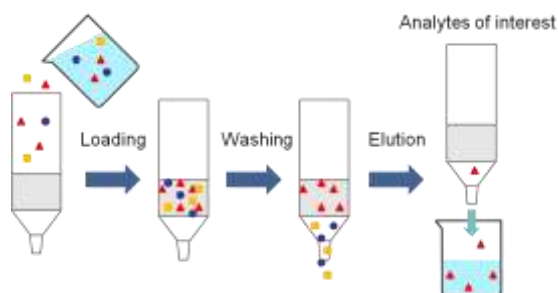
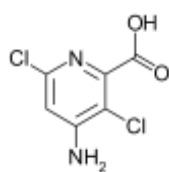
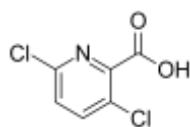


Figure 1. Typical Solid Phase Extraction process

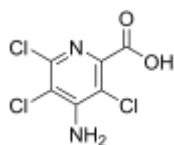
### BACKGROUND



Aminopyralid



Clopyralid



Picloram

Aminopyralid, Clopyralid and Picloram are herbicides that belong to picolinic acid family.

Maximum residue levels in cereals have been set at 0.1 to 5 milligrams per kilograms by the European Commission (Reg. (EU) 2016/1 (Picloram), Reg. (EU) No 322/2012 (Clopyralid) and Reg. (EU) 2017/171 (aminopyralid) amending the annexes of Reg. 396/2005).

**AFFINIMIP® SPE Picolinic Herbicides** has been used for purification and analysis of the three compounds in cereals (barley). Good recoveries were observed (>80%) with a good repeatability (< 10%).

### PROTOCOLE OF PURIFICATION

Cereals (barley) are milled with steel balls. 3 grams are then mixed with 100 mL of water and shaken by magnetic stirring during 60 minutes. The solution is centrifuged at 3000 RPM during 10 minutes and the supernatant is filtered through 0.45µm filter.

### SPE PROCESS

#### Equilibration

- 2 mL Acetonitrile
- 1 mL Ultrapure water

#### Loading

- 5 mL of spiked extract

#### Washing of interferences

- 1 mL Ultrapure water

#### Drying 1 min under vacuum

#### Washing of interferences

- 1 mL Acetonitrile

#### Elution

- 3 mL Ethyl Acetate with 2% Trifluoroacetic acid

Elutions are then evaporated under nitrogen stream during 20 minutes and dissolved in mobile phase.

### ANALYSIS

HPLC was performed on an UltiMate 3000 with a Hypersil Gold 150mm\*2.1mm 3 µm particle size with a guard column (Hypersil Gold 150\*2.1 mm) at 30°C. Samples were maintained at 10°C and the injection volume was 20 µL. The separation was carried out using a gradient (see table 1) at a flow rate of 0.3mL/min.

**Table 1.** HPLC gradient for the analysis.

Time (min)	Water + 0.1% Formic acid	ACN +0.1% Formic acid
0	97	3
1	97	3
3	42	58
5	42	58
6	97	3
10	97	3

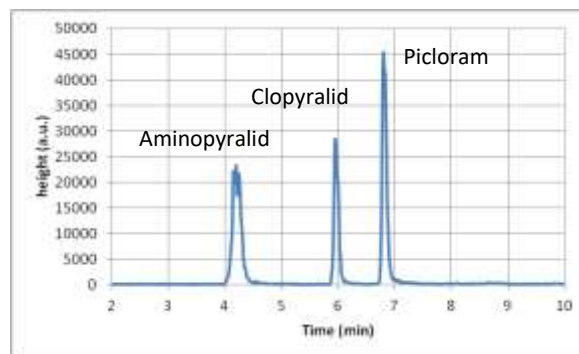
The detection system was a Qtrap 4000 Mass spectrometer used in MRM mode

**Table 2.** MRM transitions for the analysis

Analyte	Q1	Q3	DP (V)	EP (V)	CE (V)	CXP (V)
Aminopyralid Q	207	161	55	10	33	12
Aminopyralid q	207	134	55	10	45	10
Clopyralid Q	192	146	55	10	33	10
Clopyralid q	192	110	55	10	51	6
Picloram Q	241	213	55	10	29	4
Picloram q	241	185	55	10	33	4

**Mass parameters:**

Ion source: ESI Positive  
 Curtain gas: 20  
 Collision gas: High  
 IonSpray voltage: 4500 V  
 Source temperature: 550°C  
 GS1: 50  
 GS2: 50

**RESULTS**
**Figure 2.** Typical chromatogram obtained at 50µg/L.

**Table 3.** Recovery yields and repeatability (n=4) at a concentration of 333 µg/Kg

Analyte	Recovery (%)	RSDr (%) (n=4)
Aminopyralid	87.8	7
Clopyralid	82.7	4
Picloram	81.2	8

- ✓ **Very easy protocol**
- ✓ **Good Recovery (> 80%)**
- ✓ **Good repeatability (RSDr < 10%)**

**Product references**

- **AFFINIMIP® SPE Picolinic Herbicides – 6 mL**  
 FS115-02B for 25c/box – 6 mL  
 FS115-03B for 50c/box – 6 mL