

Application Note



A fast method for simultaneous analysis of 21 chlorinated acid herbicides in water with **AttractSPE® Disks Anion Exchange - SR**



This application note describes a rapid and quantitative analysis of 21 chlorinated acid herbicides in large water volumes using **AttractSPE® Disks - Anion Exchange - SR** (Table 1). Acid herbicides analyses have been historically performed using derivatization as mentioned in US EPA method 8151. However, the procedure is very complex and time consuming. **AttractSPE® Disks - Anion Exchange - SR** offers an effective alternative for the analysis of these molecules without any derivatization. In addition, European directive 98/83/CE defines an individual pesticide limit of 0.1 µg/L in drinking water. In this application note, this threshold was easily reached thanks to the use of **Attract®SPE Disks**.

Attract®SPE Disks are thin, dense, soft and uniform extraction SPE membranes allowing the rapid loading of large sample volumes thanks to a fast flow rate and without any channeling. Our innovative SPE disks have a high surface area of exchange that allows the best interactions with analytes to obtain excellent recoveries (>80%). **AttractSPE® Disks** reduces extraction time with large sample volumes while ensuring a high enrichment of the analytes. Several formats and chemistries are available to best suit each application.

The most important benefit of this method for large water volumes is time saving. This method allows a sample preparation step in less than 30 min instead of at least 3 hours using SPE cartridges.

Moreover, the use of AttractSPE® Disks avoids the clogging of the SPE column by particles in suspension, a frequent problem during environmental water samples analysis.

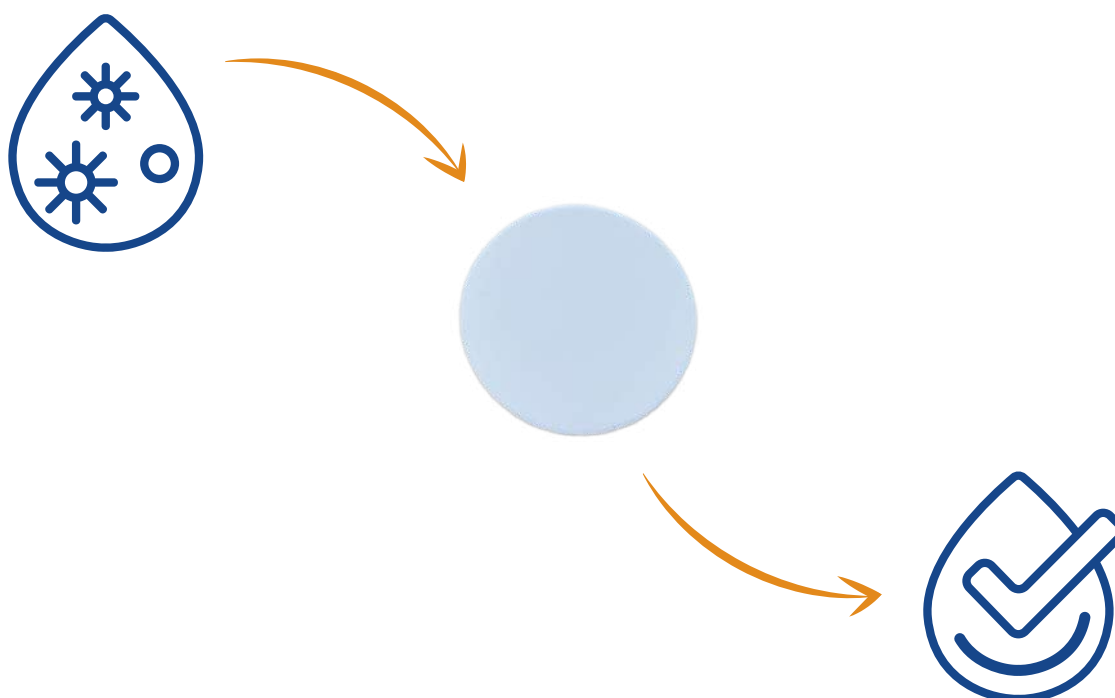
AttractSPE® Disks is as well the perfect membrane to use for the passive sampler like Chemcatcher® or any disk passive samplers thanks to a very good hold and a great ease to use.

Table 1. List of the 21 tested chlorinated acid herbicides

COMPOUNDS	CAS NUMBER	COMPOUNDS	CAS NUMBER
AMINOPYRALID	150114-71-9	3,5 DICHLORO BENZOIC ACID	51-36-5
CLOPYRALID	1702-17-6	DICHLORPROP	120-36-5
PICLORAM	1918-02-1	2,4,5-T	93-76-5
CHLORAMBEN	133-90-4	DALAPON	75-99-0
DICAMBA	1918-00-9	IOXYNIL	1689-83-4
4-NITROPHENOL	100-02-7	2,4-DB	94-82-6
FLUROXYPYR	69377-81-7	FENOPROP	93-72-1
BENTAZONE	25057-89-0	ACIFLUORFEN	50594-66-6
2,4-D	94-75-7	DINOSEB	88-85-7
BROMOXYNIL	1689-84-5	PENTACHLOROPHENOL	87-86-5
TRICLOPYR	55335-06-3		

47mm **AttractSPE®** Disks - Anion Exchange - SR (SAX) were used for this study

Loading solution: One liter of tap water is spiked at 100ng/L with 21 acid herbicides, and 50 µL of NH₃ 30% is added to obtain a pH above 7. One liter of tap water (not spiked) was also performed as a blank control.



PURIFICATION PROTOCOL

Place the **AttractSPE® Disks – Anion Exchange – SR** onto the SPE disk manifold.

Note: A glass microfiber (1 µm or 3 µm) can be added on top of the disk to prevent clogging from particulates in the water sample.

CONDITIONING/EQUILIBRATION

1. 20 mL Acetone (soak disk for 30 seconds)
2. 20 mL Isopropanol (soak disk for 30 seconds)
3. 20mL Methanol (soak disk for 30 seconds)
4. 20 mL ultrapure water

LOADING

1. 1 L at 50-75 mL/min

WASHING

1. 20mL ultrapure water
2. Dry disk 1 minute under full vacuum

ELUTION

1. 20 mL 3% formic acid in methanol freshly (soak disk for 30 seconds)
2. 20 mL 3% formic acid in methanol

ANALYSIS

The eluate was then agitated and diluted (1:4 ratio) with ultrapure water prior to analysis.

Note: The eluate can also be concentrated by evaporation to improve the limit of quantification.

AttractSPE® Disks **SOFT MEMBRANE WITH** **HIGH CAPACITY**



After the cleanup procedure, the molecules were simultaneously analyzed by LC-MS/MS. The results obtained are presented in Table 2.

COMPOUNDS	PRESENCE IN BLANK	% RECOVERY	% RSDr (n = 3)
AMINOPYRALID	ND	86	7
CLOPYRALID	ND	91	5
PICLORAM	ND	88	4
CHLORAMBEN	ND	91	2
DICAMBA	ND	91	5
4-NITROPHENOL	ND	85	5
FLUROXYPYR	ND	93	2
BENTAZONE	ND	91	3
2,4-D	ND	86	2
BROMOXYNIL	ND	89	5
TRICLOPYR	ND	89	7
3,5 DICHLOROBENZOIC ACID	ND	90	1
DICHLORPROP	ND	86	6
2,4,5-T	ND	83	7
DALAPON	ND	86	4
IOXYNIL	ND	84	6
2,4-DB	ND	85	11
FENOPROP	ND	97	8
ACIFLUORFEN	ND	83	3
DINOSEB	ND	88	4
PENTACHLOROPHENOL	ND	84	3

Table 2. Percent recovery of 21 acid herbicides at a concentration of 100 ng/L in tap water after the **AttractSPE® Disks - Anion Exchange - SR** cleanup. (ND : Not detected)

Recoveries ranging from 80% to 97% for the 21 molecules were observed, demonstrating the success of the purification method using **AttractSPE® Disks - Anion Exchange - SR**

Table 3. Conditions of picolinic herbicides analysis with LC-MS/MS.

LC CONDITIONS	MS CONDITIONS	TIME (MIN)	% WATER 0.1% ACETIC ACID	% ACETONITRILE 0.1% ACETIC ACID
LC Dionex U3000	Qtrap 4000 ESI+ MS/MS	0	90	10
Column : SilactHPLC LC.A 150x2.1mm (3µm) at 40°C)	Curtain gas : 30	0.5	90	10
	CAD: High	15	10	90
Injection volume : 20 µL	IS : 4500 V	20	10	90
T° sampler : 15°C	Temperature : 400°C	21	90	10
Flow rate : 0.2 mL/min	GS1/GS2 : 30/30	26	90	10

ANALYTE	RETENTION TIME (MIN)	Q1	Q3	CE (V)
Aminopyralid	3.6	205.0	160.9	-12
Clopyralid	5.1	190.0	145.7	-14
Picloram	7.1	238.9	194.8	-14
Chloramben	9.8	204.0	159.9	-12
Dicamba	10.3	219.0	174.9	-10
4-nitrophenol	11.1	138.0	108.0	-24
Fluroxypyr	11.5	253.0	195.0	-16
Bentazone	12.3	239.0	131.8	-36
2,4-D	12.9	247.0	161.0	-12
Bromoxynil	13.5	275.9	78.8	-48
Triclopyr	13.6	255.9	197.8	-16
3,5 dichlorobenzoic acid	13.8	189.0	144.9	-16
Dichlorprop	14.0	233.0	160.8	-20
2,4,5-T	14.0	252.9	194.8	-18
Dalapon	14.1	141.0	35.1	-36
Ioxynil	14.4	369.9	127.0	-50
2,4-DB	14.7	247.0	161.0	-12
Fenoprop	15.0	266.9	194.7	-16
Acifluorfen	15.1	360.0	315.9	-14
Dinoseb	17.1	239.0	192.8	-34
Pentachlorophenol	17.3	264.8	35.0	-48

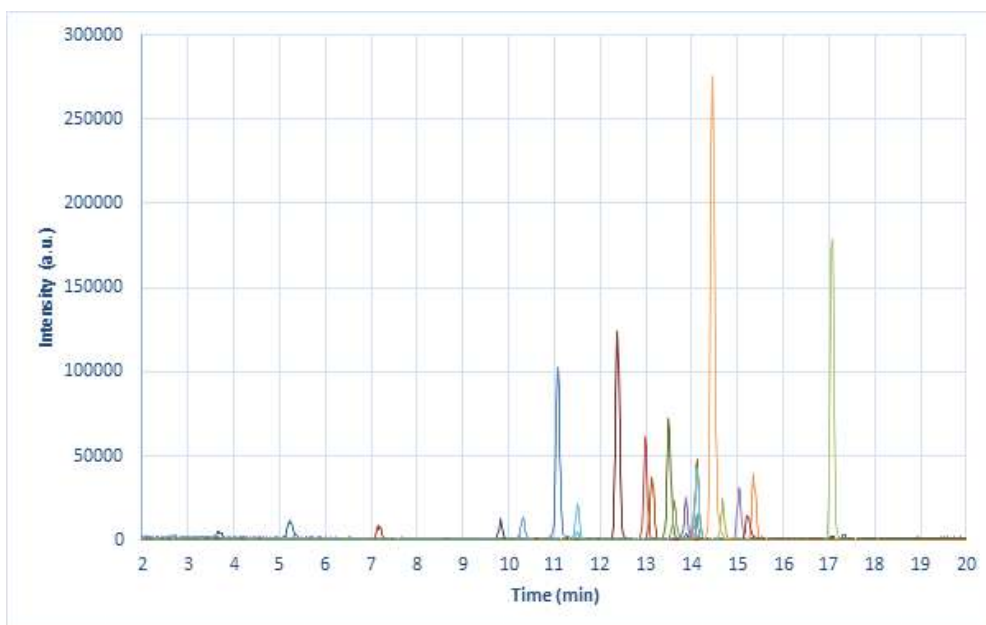


Figure 1. LC-MS/MS chromatogram of acid herbicides at 1 µg/L after cleanup with **AttractSPE® Disks – Anion Exchange – SR**.

Conclusion

AttractSPE® Disks – Anion Exchange - SR have shown excellent performances for the concentration and analysis of 21 chlorinated acid herbicides with excellent recovery yields above 80%. SPE disk format allowed a fast treatment of large sample volumes (~20-25 min). Furthermore, an excellent repeatability was obtained. The method makes possible a 1000-times concentration of samples.

AttractSPE® Disks – Anion Exchange – SR

- *SPE-Disks-AN-25.T1.40 for 40/pk – 25mm*
- *SPE-Disks-AN-47.T1.20 for 20/pk – 47mm*
- *SPE-Disks-AN-90.T1.10 for 10/pk – 90mm*

AttractSPE® Prefilter Glassfiber for 47mm disks

(also available for other diameters)

- *PF-GF-50.T1.47.1 for 50/pk – 1µm*
- *PF-GF-50.T1.47.3 for 50/pk – 3 µm*

SPE Disks manifold 47mm (also available for 90mm):

- *1 station ACC-DISKSPE-G47-1*
- *3 stations ACC-DISKSPE-G47-3*
- *6 stations ACC-DISKSPE-G47-6*

Related Products

AttractSPE® Disks Passive Sampler Anion exchange - SR - 10/pk

- DBPS.AN.90.40.kit.10

AFFINIMIP® SPE Picolonic herbicides

6mL – 50/pk

- FS115-03B

HPLC column: SilactHPLC LC.A-150.2.1

150 x 2.1mm, 3 µm 1 unit

- LC.A-150.2.1

