

METHOD STATEMENT



Determinand:

Dissolved phenoxy acid herbicides, benzoic acid herbicides, benzonitrile herbicides and pentachlorophenol, (determined as free acids)

Matrix:

Surface waters, Effluents, Leachates and Groundwater.

Principle of Method:

The free acid compounds are extracted from acidified aqueous solution using styrene-divinyl benzene (SDVP) solid phase extraction (SPE) cartridges. The compounds are eluted from the cartridges with ethyl acetate and reacted with diazomethane to form the methyl derivatives. The derivatives are quantified by gas chromatography with mass spectrometry detection (GC-MS).

Sampling and Sample Preparation:

Samples should be stored between $3\pm 2^{\circ}\text{C}$.

Extracts must be stored in a refrigerator between 2 and 8°C if they cannot be analysed on the day that they are vialled

Samples are stable for 14 days (In-House Data) from sampling

Interferences:

Any substance, or substance yielding a methyl derivative, with a corresponding GC retention time and with the same ions as those being monitored, will interfere.

Performance of Method:

Range of Application: 50 ng/l – 5000 ng/l without dilution

Normal Reporting Level: 50 ng/l (Mecoprop 40ng/l)

Determinand	LOD ng/l	MRL ng/l	Low Std		High Std	
			%Bias	%RSD	%Bias	%RSD
Clopyralid	17.63	50	1.62	4.55	-0.59	3.96
Dicamba	23.93	50	-1.27	5.74	-0.17	3.24
2,3,6-TBA	22.88	50	-1.56	5.01	-0.13	3.06
Mecoprop	27.46	40	-2.23	4.38	0.00	3.10
MCPA	29.55	50	-1.96	4.24	-0.39	3.50
Dichlorprop	26.40	50	-1.12	3.97	0.14	2.58
2,4-D	28.62	50	-0.85	4.08	-0.30	3.49
Triclopyr	20.96	50	-2.53	4.86	-1.26	5.52
Fenoprop	33.04	50	-3.97	5.97	-1.45	5.94
MCPB	23.63	50	-4.09	5.85	-2.17	5.61
2,4,5-T	34.29	50	0.08	4.61	-0.99	4.87
Fluroxypyr	32.25	50	0.05	6.46	-1.24	6.53
2,4-DB	22.74	50	-3.85	6.19	-1.12	3.91
Bentazone	13.64	50	-3.20	3.66	-0.13	4.28
Benazolin	32.42	50	-1.56	4.68	0.80	2.83
Bromoxynil	16.73	50	-2.15	3.63	1.36	4.34
Ioxynil	26.89	50	-3.05	12.59	1.99	13.40
Pentachlorophenol	27.97	50	-1.00	3.47	-0.85	1.66

METHOD STATEMENT



20% Spiked Sample Recoveries

Determinand	Finham FE		Wolston FE		Trade Effluent	
	%Rec.	%RSD	%Rec.	%RSD	%Rec.	%RSD
Clopyralid	103.78	7.18	100.61	6.96	101.05	7.98
Dicamba	96.07	6.68	97.18	8.52	93.91	8.24
2,3,6-TBA	95.32	6.52	96.20	8.04	93.99	6.92
Mecoprop	95.70	6.51	98.15	6.96	95.91	6.18
MCPA	99.76	6.47	98.92	5.37	99.90	4.99
Dichlorprop	97.22	4.88	99.00	6.09	96.87	4.75
2,4-D	102.99	4.44	103.47	4.66	99.08	3.98
Triclopyr	98.28	6.55	98.44	6.52	94.87	5.03
Fenoprop	96.73	6.33	97.52	6.34	94.58	5.06
MCPB	90.93	8.19	97.07	5.90	99.26	9.89
2,4,5-T	100.41	5.39	101.15	4.54	98.64	5.16
Fluroxypyr	108.38	6.01	111.45	11.47	106.73	8.5
2,4-DB	93.38	7.44	97.95	6.09	100.17	4.71
Bentazone	96.83	4.44	97.62	5.15	96.88	4.12
Benazolin	98.50	5.82	98.81	6.06	96.02	7.57
Bromoxynil	97.09	5.06	98.90	6.53	99.90	5.21
Ioxynil	105.00	10.71	107.06	8.09	107.54	9.20
Pentachlorophenol	94.21	3.88	94.25	6.62	97.54	3.19

Determinand	Groundwater		Landfill Leachate		Surface Water	
	%Rec.	%RSD	%Rec.	%RSD	%Rec.	%RSD
Clopyralid	97.83	8.88	94.60	9.36	93.04	6.64
Dicamba	89.97	7.93	91.96	8.08	92.55	8.52
2,3,6-TBA	90.00	8.14	92.07	8.87	92.35	8.85
Mecoprop	93.24	6.96	93.97	8.12	94.19	8.46
MCPA	96.56	5.84	96.06	7.05	94.72	8.57
Dichlorprop	94.46	6.85	96.25	8.05	94.40	8.10
2,4-D	94.76	4.67	96.06	6.13	95.17	6.95
Triclopyr	101.22	4.87	100.17	7.23	95.29	7.11
Fenoprop	97.46	6.21	98.02	7.20	96.15	7.50
MCPB	94.73	8.27	95.67	9.77	92.91	10.27
2,4,5-T	97.68	4.71	98.69	6.14	96.07	7.21
Fluroxypyr	103.49	7.10	97.66	6.18	101.59	5.07
2,4-DB	99.30	7.24	100.01	7.42	97.99	9.07
Bentazone	94.36	6.89	95.32	7.30	94.66	8.32
Benazolin	92.66	7.03	89.59	6.96	95.23	6.87
Bromoxynil	93.80	7.73	96.04	7.85	94.05	8.96
Ioxynil	99.96	10.31	100.83	10.35	96.77	9.60
Pentachlorophenol	93.36	8.25	94.83	9.25	92.96	9.21

METHOD STATEMENT



80% Spiked Sample Recoveries

Determinand	Finham FE		Wolston FE		Trade Effluent	
	%Rec.	%RSD	%Rec.	%RSD	%Rec.	%RSD
Clopyralid	103.40	3.91	97.23	4.77	95.58	4.93
Dicamba	95.55	3.91	95.25	5.34	93.86	3.98
2,3,6-TBA	96.62	4.03	95.34	5.36	94.20	4.11
Mecoprop	97.34	3.97	97.11	5.14	96.08	3.55
MCPA	100.00	3.45	97.83	4.31	98.48	3.30
Dichlorprop	97.76	3.34	97.46	4.25	96.78	2.61
2,4-D	100.32	3.16	98.76	2.82	99.16	3.10
Triclopyr	97.04	5.41	96.80	5.05	95.82	4.68
Fenoprop	96.72	5.55	96.04	6.48	95.77	5.11
MCPB	92.67	5.80	94.82	5.10	96.19	4.28
2,4,5-T	98.18	4.88	96.21	4.37	98.47	4.18
Fluroxypyr	106.43	8.41	102.62	7.11	101.20	7.43
2,4-DB	94.69	4.26	96.79	4.17	97.76	3.87
Bentazone	96.26	3.72	96.16	4.45	95.72	3.21
Benazolin	98.68	3.38	96.67	5.34	96.22	2.22
Bromoxynil	98.07	3.87	98.41	4.41	100.05	4.45
Ioxynil	104.86	9.26	105.06	10.55	106.36	8.95
Pentachlorophenol	94.65	3.71	94.52	3.47	97.80	3.00

Determinand	Groundwater		Landfill Leachate		Surface Water	
	%Rec.	%RSD	%Rec.	%RSD	%Rec.	%RSD
Clopyralid	99.66	8.59	98.38	4.93	95.17	5.45
Dicamba	92.61	4.62	95.34	4.70	95.23	2.99
2,3,6-TBA	92.21	5.54	95.55	4.84	95.34	3.08
Mecoprop	97.38	5.40	97.83	4.40	98.03	4.57
MCPA	99.15	3.96	99.90	3.70	99.17	3.85
Dichlorprop	97.87	3.90	98.25	3.91	98.36	3.32
2,4-D	98.91	3.20	98.87	3.65	99.23	3.23
Triclopyr	99.92	3.14	101.67	4.39	98.60	2.85
Fenoprop	98.65	3.68	100.52	4.40	98.71	3.03
MCPB	96.81	4.86	98.68	4.96	97.26	3.84
2,4,5-T	99.35	4.15	101.76	4.67	99.64	3.54
Fluroxypyr	104.08	6.27	104.12	3.96	103.27	5.61
2,4-DB	99.31	4.32	99.61	4.06	99.25	3.32
Bentazone	95.39	3.80	97.54	4.40	96.22	2.76
Benazolin	95.96	4.44	96.46	4.00	98.27	5.55
Bromoxynil	96.28	4.02	99.24	5.09	95.19	13.01
Ioxynil	102.62	7.48	103.70	8.02	100.71	10.83
Pentachlorophenol	98.46	4.66	99.98	3.89	98.93	3.37

METHOD STATEMENT



Determinand	Untreated Sewage	
	%Rec.	%RSD
Clopyralid	97.70	7.3
Dicamba	96.41	7.35
2,3,6-TBA	98.61	7.02
Mecoprop	94.89	6.95
MCPA	98.26	6.18
Dichlorprop	96.59	6.40
2,4-D	99.51	6.72
Triclopyr	99.46	5.73
Fenoprop	98.04	5.80
MCPB	96.02	5.32
2,4,5-T	98.50	5.91
Fluroxypyr	106.53	9.57
2,4-DB	97.19	5.55
Bentazone	96.37	6.28
Benazolin	98.75	9.22
Bromoxynil	88.22	15.0
Ioxynil	94.85	8.91
Pentachlorophenol	99.70	3.06

Uncertainty of Measurement

The reported uncertainty is an expanded uncertainty calculated using a coverage factor of 2, which gives a level of confidence of approximately 95%.

Determinand	Uncertainty of Measurement %
Clopyralid	16.28
Dicamba	17.62
2,3,6-TBA	17.24
Mecoprop	13.09
MCPA	11.41
Dichlorprop	12.64
2,4-D	12.35
Triclopyr	17.89
Fenoprop	18.27
MCPB	20.48
2,4,5-T	17.17
Fluroxypyr	23.32
2,4-DB	16.60
Bentazone	23.88
Benazolin	15.32
Bromoxynil	12.12
Ioxynil	24.45
Pentachlorophenol	14.29

METHOD STATEMENT



References:

HP 6890 Series Gas Chromatograph Operating Manual Vol. 1. General Information G3430 90011

Environmental GCMSD Instrument and Chemstation Operation Vols. 1 and 2. G 1701 BA.

In-house developed method