

# METHOD STATEMENT



## Determinand:

Volatile Fatty Acids

(Acetic acid, propionic acid, n-butyric acid, isobutyric acid, n-valeric acid, isovaleric acid, n-caproic acid, isocaproic acid and methacrylic acid)

## Matrix:

Sewage sludge, leachates, effluents, surface waters and groundwaters.

## Principle of Method:

The sample is centrifuged, if necessary, and treated with formic acid to minimise adsorption effects on the gas chromatographic column (this also stabilises the liquor and prevents further biological activity, which would produce additional fatty acids). The individual acids present in the mixture are determined by gas chromatography with flame ionisation detection (GC-FID), using internal standardisation.

## Sampling and Sample Preparation:

Samples are fixed with formic acid as soon as possible after receipt of the samples. If dilution is necessary, the fixed subsample is used, not the sample as received at the laboratory, as degradation will have taken place.

Samples are stable for 5 days (In-House Data) from sampling.

## Interferences:

Any substance detected by the FID with the same retention time as an individual VFA will interfere.

## Performance of Method:

Range of Application: 10mg/l to 500mg/l without dilution for acetic and propionic  
10mg/l to 100mg/l without dilution for all other acids

Normal Reporting Level: 10mg/l as individual acids (5mg/l as carbon)  
20mg/l as total volatile acids (10mg/l as carbon)

## LOD, Precision and Bias

Determinand	LOD mg/l	Waters				Sludges			
		Low Std*		High Std*		Low Std*		High Std*	
		% Bias	% RSD	% Bias	% RSD	% Bias	% RSD	% Bias	% RSD
Acetic Acid	5.36	0.45	4.37	-2.09	8.42	0.45	4.37	-2.09	8.42
Propionic Acid	2.51	1.28	4.84	-1.20	8.14	1.28	4.84	-1.20	8.14
Isobutyric Acid	0.51	1.41	4.93	-0.46	7.74	1.41	4.93	-0.46	7.74
n-Butyric Acid	0.63	1.44	5.04	-0.57	8.41	1.44	5.04	-0.57	8.41
Isovaleric Acid	0.44	1.65	4.16	-0.48	8.05	1.65	4.16	-0.48	8.05
Methacrylic Acid	0.60	0.59	5.57	-1.41	7.85	0.59	5.57	-1.41	7.85
n-Valeric Acid	0.45	1.07	4.66	0.27	7.74	1.07	4.66	-0.27	7.74
Isocaproic Acid	0.48	0.97	4.39	-0.20	7.45	0.97	4.39	-0.20	7.45
n-Caproic Acid	0.99	0.61	4.35	-0.03	7.32	0.61	4.35	-0.03	7.32

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## Spike Recoveries from Matrix Waters

Determinand	Treated Effluent		Groundwater		Landfill Leachate	
	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD
Acetic Acid	97.7	4.73	98.1	4.58	98.0	7.65
Propionic Acid	99.3	5.45	98.9	4.09	99.1	7.46
Isobutyric Acid	99.2	6.83	99.7	4.25	99.5	7.40
n-Butyric Acid	99.1	4.99	99.4	4.25	99.5	7.73
Isovaleric Acid	99.5	4.63	99.82	4.34	99.6	7.31
Methacrylic Acid	98.9	4.64	99.1	4.46	99.2	7.35
n-Valeric Acid	99.4	4.66	99.8	4.41	99.6	7.35
Isocaproic Acid	99.6	4.58	99.7	4.49	99.5	7.11
n-Caproic Acid	99.6	4.29	99.6	4.58	99.6	6.93

Determinand	Soil Leachate		Surface Water		Trade Effluent	
	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD
Acetic Acid	99.2	6.66	98.3	7.03	97.5	8.31
Propionic Acid	100.2	6.37	99.1	6.89	98.3	8.08
Isobutyric Acid	100.9	6.39	99.6	7.01	98.6	8.11
n-Butyric Acid	100.5	6.38	99.3	7.19	98.1	8.36
Isovaleric Acid	100.8	6.10	99.6	6.75	98.6	7.93
Methacrylic Acid	100.3	6.24	99.2	6.94	98.1	8.09
n-Valeric Acid	100.7	6.08	99.6	6.69	98.5	7.96
Isocaproic Acid	100.7	6.01	99.5	6.77	98.4	7.81
n-Caproic Acid	100.7	5.71	99.6	6.60	98.5	7.61

Determinand	Untreated Sewage	
	% Rec.	% RSD
Acetic Acid	101.0	5.01
Propionic Acid	102.0	5.00
Isobutyric Acid	102.1	4.72
n-Butyric Acid	102.0	4.83
Isovaleric Acid	102.2	3.47
Methacrylic Acid	101.9	4.74
n-Valeric Acid	102.1	4.75
Isocaproic Acid	101.31	4.81
n-Caproic Acid	102.0	4.59

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## Spike Recoveries from Matrix Sludges

Determinand	Sewage Sludge	
	% Recovery	% RSD
Acetic Acid	95.6	7.22
Propionic Acid	96.5	7.18
Isobutyric Acid	96.8	7.04
n-Butyric Acid	96.7	7.25
Isovaleric Acid	96.7	6.96
Methacrylic Acid	96.5	6.98
n-Valeric Acid	96.8	7.02
Isocaproic Acid	96.8	6.77
n-Caproic Acid	96.9	6.53

## Uncertainty of Measurement (UoM)

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

Determinand	UoM (%)	
	Waters	Sludges
Acetic Acid	18.87	18.53
Propionic Acid	18.83	17.94
Isobutyric Acid	19.43	18.08
n-Butyric Acid	19.43	18.44
Isovaleric Acid	19.31	18.05
Methacrylic Acid	19.02	18.58
n-Valeric Acid	19.29	18.58
Isocaproic Acid	18.65	18.35
n-Caproic Acid	18.85	19.28

## References:

Determination of Volatile Fatty Acids in Sewage Sludge, 1979, HMSO. ISBN 0 11 751462 4. Method A