METHOD STATEMENT

Determinand:
The Six World Health Organisation (WHO) Polycyclic Aromatic Hydrocarbons (PAHs).
- Fluoranthene
- Benzo(b)fluoranthene *
- Benzo(k)fluoranthene
- Benzo(a)pyrene * also known as Benzo(def)chrysene
- Benzo(ghi)perylene
- Indeno(123 cd)pyrene *

Matrix:
Sample Types: Raw and Potable waters.

Principle of Method:
PAHs are extracted by solvent extraction prior to examination and quantification by HPLC using fluorescence detection. The method is based upon the method for six specific PAHs in water, using High Performance Liquid Chromatography, from the Standing Committee of Analysts booklet 1985. Quantitation is based on an internal standardisation procedure
The concentrations of PAHs in drinking water become important when related to the health effects of these compounds. PAHs are known to leach out of coal tar that was historically used for protection of iron water mains. Some of these compounds are known carcinogens; consequently, the World Health Organisation and EEC have set an upper total limit of 200 ng/l for the six PAHs of interest in domestic waters. The six PAHs of interest are:
- Fluoranthene
- Benzo(b)fluoranthene *
- Benzo(k)fluoranthene
- Benzo(a)pyrene * also known as Benzo(def)chrysene
- Benzo(ghi)perylene
- Indeno(123 cd)pyrene *

Substances marked * are known carcinogens.
Note: the maximum permissible concentration for Benzo(a)pyrene in potable waters is 10 ng/l.

Sampling and Sample Preparation:
Samples are taken in 1 litre amber or green glass bottles designated as "PAH" (ALE220), with PTFE lined screw tops. These bottles are preserved with 1ml of 160g/l Sodium Thiosulphate solution. Bottles should be filled completely and stored in a refrigerator at 3±2°C, upon receipt at the laboratory. Samples should be extracted within 21 days from sampling.
Extracts are preferably kept in a fridge if analysis does not take place immediately and analysed as soon as possible, however being kept at room temperature for up to three days has no adverse effect on them. Random samples are analysed for the presence of residual chlorine as a check on the presence of preservative in the sample according to our guidelines.

Interferences
Any material, which fluoresces, quenches fluorescence, or has similar chromatographic properties to the specified PAH will interfere in the method.

Performance of Method:

Range of Application:

Fluoranthene	LOQ - 160ng/l
Benzo(b)fluoranthene	LOQ - 160ng/l

Benzo(k)fluoranthene LOQ - 80ng/l
Benzo(a)pyrene LOQ - 160ng/l
Benzo(ghi)perylene LOQ - 160ng/l
Indeno(123 cd)pyrene LOQ - 160ng/l
Any extracts giving peak height results above those in the level 4 calibration standard should be diluted onto linear range.

Limit of Quantification, Recoveries of Compounds and Uncertainty of measurement:

Instrument 1, HPLC2:

Determinand	**Direct Standards**				**Elvington Treated Water (Hard Hardness)**		
	Low Standard		High Standard		Spike		
	Recovery	RSD	Recovery	RSD	Recovery	RSD	UoM
Fluoranthene	98.20%	3.10%	98.00%	4.10%	92.90%	5.50%	± 16.87%
Benzo(b)fluoranthene	100.60%	2.50%	100.10%	3.60%	100.20%	2.80%	± 7.56 %
Benzo(k)fluoranthene	100.00%	2.40%	99.90%	3.70%	100.50%	3.10%	± 8.30 %
Benzo(a)pyrene	98.50%	2.80%	98.90%	3.50%	101.00%	3.00%	± 8.43 %
Benzo(ghi)pyrene	100.00%	2.30%	99.60%	3.50%	102.80%	2.90%	± 8.79 %
Indeno(123 cd)pyrene	100.20%	2.70%	100.30%	3.70%	100.70%	3.10%	± 8.93 %

Instrument 1, HPLC3:

Determinand	**Direct Standards**				**Elvington Treated Water (Hard Hardness)**		
	Low Standard		High Standard		PCV Spike		
	Recovery	RSD	Recovery	RSD	Recovery	RSD	UoM
Fluoranthene	100.82%	6.12%	100.33%	3.60%	102.02%	4.00%	± 19.69%
Benzo(b)fluoranthene	102.22%	5.50%	101.32%	3.67%	103.05%	3.32%	± 16.77%
Benzo(k)fluoranthene	104.13%	5.66%	102.09%	3.43%	103.91%	3.52%	± 16.40%
Benzo(a)pyrene	102.53%	6.16%	101.28%	3.63%	102.75%	3.46%	± 15.41%
Benzo(ghi)pyrene	101.62%	6.15%	101.03%	3.66%	103.04%	3.67%	± 14.21%
Indeno(123 cd)pyrene	102.95%	5.61%	100.50%	3.78%	102.29%	3.45%	± 14.73%

Sum of 4 PAH is the summation of Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(ghi)perylene and Indeno(1,2,3-Cd)pyrene.
*DWI guidelines state that individual PAHs not detected are assigned a value of 0 for the purposes of calculating the total PAH values.

The highest LOQ has been applied across all instruments:

Determinand	**WHPLC2 Limit of Quantification (ng L^{-1})**	**WHPLC3 Limit of Quantification (ng L^{-1})**	**METHOD (Standardised) LOQ (ng L^{-1})**
Fluoranthene	0.77	1.03	**1.03**
Benzo (b) fluoranthrene	0.33	0.70	**0.70**
Benzo (k) fluoranthrene	0.44	0.99	**0.99**
Benzo (a) pyrene	0.42	0.39	**0.42**
Benzo (ghi) perylene	0.77	0.74	**0.77**
Indeno (1,2,3cd) pyrene	1.04	0.90	**1.04**

References:

The PAH method from the Standing Committee of Analysts 1985, Method A, p. 9.