SCHEDULE 4 Regulation 12

Sampling and Analysis

PART 1

General

Samples: general

1. The Department must ensure that each sample taken in accordance with a monitoring programme is—

(a) representative of the water at the sampling point at the time of sampling;

(b) not contaminated in the course of being taken;

(c) for the chemical parameters copper, lead and nickel taken without prior flushing and is a random daytime sample of one litre volume;

(d) for chemical parameters in the distribution network be undertaken in accordance with ISO 5667-5, other than where the sample is taken from a consumer's tap;

(e) for microbiological parameters taken and handled according to EN ISO 19458, sampling purpose A and B;

(f) kept at such temperature and in such conditions as will secure that there is no material alteration of a concentration, value or state of any parameter/measurement/observation for which the sample is to be analysed; and

(g) analysed as soon as may be possible after it has been taken—

(i) by a person who is competent to perform that task; and

(ii) with the use of such equipment as is suitable for the purpose.

Analysing samples

2.—(1) The Department must ensure each sample is analysed in accordance with this paragraph and that analysis methods used are validated and documented in accordance with EN ISO/IEC 17025 or other equivalent standards accepted at an international level.

(2) For each parameter specified in the first column of Table A in Part 2 of this Schedule "Table A" the method of analysis is specified in the second column of that table.

(3) For each parameter specified in the first column of Table B in Part 2 of this Schedule "Table B" the method of analysis must be capable of measuring concentrations equal to the parametric value with a limit of quantification of 30% or less of the relevant parametric value set in Schedule 1 and an uncertainty of measurement as specified in Table B.

(4) The Department must not use the uncertainty of measurement in Table B as an additional tolerance to the parametric values set in Schedule 1.

(5) For hydrogen ion, a method of analysis which is capable at the time of use of measuring a value with a trueness of 0.2 pH unit and a precision of 0.2 pH unit.

(6) The result of analysis of parameters under this regulation must be expressed using at least the same number of significant figures as for the associated parametric values in Part 1 of Schedule 1.

(7) For these purposes—

"limit of quantification" is to be calculated using an appropriate standard or sample, and may be obtained from the lowest calibration point on the calibration curve, excluding the blank; and

"measurement uncertainty" shall be estimated at the level of the parametric value, unless otherwise specified.

Authorisation of alternative methods of analysis

3.—(1) If the Department is satisfied that an alternative method of analysis is at least as reliable as a method of analysis prescribed by paragraph 2(2), it may authorise its use instead of the prescribed method.

(2) The Department shall provide the European Commission with relevant information concerning such methods authorised in paragraph 3(1) and their equivalence.

(3) Until 31 December 2019 the Department may use "trueness", "precision" and "limit of detection" as specified in Table C in Part 2 of this Schedule ("Table C") as alternative sets of performance characteristics to "limit of quantification" and "uncertainty of measurement" specified in paragraph 6 and Table B of this Schedule.

(4) For the purposes of this paragraph the method of analysis for each parameter specified in the first column of Table C must be capable of—

(a) measuring concentrations and values with the trueness and precision specified in the second and third columns of that table; and

(b) detecting the parameter at the limit of detection specified in the fourth column of that table.

(5) For hydrogen ion, a method of analysis must be capable at the time of use of measuring a value with a trueness of 0.2 pH unit and a precision of 0.2 pH unit.

(6) For these purposes—

"limit of detection" is to be calculated as—

(a) three times the relative within-batch standard deviation of a natural sample containing a low concentration of the parameter; or

(b) five times the relative within-batch standard deviation of a blank sample;

"precision" (the random error) is to be calculated as twice the standard deviation (within a batch and between batches) of the spread of results about the mean; and

"trueness" (the systematic error) is to be calculated as the difference between the mean value of the large number of repeated measurements and the true value.

(7) In the absence of an analytical method meeting the minimum performance criteria set out in sub-paragraph (3) and paragraph 2(3) the Department must ensure that monitoring is carried out using best available techniques not entailing excessive costs.

Laboratories

4. The Department must ensure that the laboratory at which samples are analysed has a system of analytical quality control in accordance with EN ISO/IEC 17025 or other equivalent standards accepted at an international level and is subjected from time to time to checking by a person who is—

(a) not under the control of either the laboratory or the Department; and

(b) approved by the Department for that purpose.

Interpretation

5. In this schedule—

"laboratory" includes any land at which samples are analysed for the purposes of these Regulations (including on-site analysis); and

"taking and analysing samples" includes taking, handling, transporting, storing and analysing samples.

PART 2

Analytical Methods and Performance Characteristics

TABLE A

Prescribed methods of analysis

(1) Parameter	*(2) Method*
Clostridium perfringens (including spores)	EN ISO 14189
Coliform bacteria	EN ISO 9308-1 or EN ISO 9308-2
Colony count 22°C-enumeration of culturable microorganisms	EN ISO 6222
Enterococci	EN ISO 7899-2
Escherichia coli (*E. coli*)	EN ISO 9308-1 or EN ISO 9308-2
Pseudomonas aeruginosa	EN ISO 16266

TABLE B

Minimum performance characteristic: "uncertainty of measurement"

(1) Parameter[(1)]	*(2) Uncertainty of measurement (% of parametric value, except pH)*[(2)]
Aluminium	25
Ammonium	40
Antimony	40
Arsenic	30
Benzo(a)pyrene[(3)]	50
Benzene	40
Boron	25
Bromate	40
Cadmium	25
Chloride	15
Chromium	30
Colour	20
Conductivity	20
Copper	25

(1) Parameter[1]	*(2) Uncertainty of measurement (% of parametric value, except pH)*[2]
Cyanide[4]	30
1,2-dichloroethane	40
Fluoride	20
Hydrogen ion concentration pH (expressed in pH units)[5]	0.2
Iron	30
Lead	25
Manganese	30
Mercury	30
Nickel	25
Nitrate	15
Nitrite	20
Oxidisability[6]	50
Pesticides[7]	30
Polycyclic aromatic hydrocarbons[8]	50
Selenium	40
Sodium	15
Sulphate	15
Tetrachloroethene[9]	30
Tetrachloromethane	30
Trichloroethene[9]	40
Trihalomethanes: total[8]	40
Total organic carbon[10]	30
Turbidity[11]	30

(1) Acrylamide, epichlorohydrin and vinyl chloride to be controlled by product specification.

(2) Uncertainty of measurement is a non-negative parameter characterising the dispersion of the quantity values being attributed to a measurand, based on the information used. The performance criterion for measurement uncertainty (k = 2) is the percentage of the parametric value stated in the table or better. Measurement uncertainty must be estimated at the level of the parametric value, unless otherwise specified.

(3) If the value of uncertainty of measurement cannot be met, the best available technique should be selected (up to 60%).

(4) The method determines total cyanide in all forms.

(5) Values for trueness, precision and uncertainty of measurement are expressed in pH units.

(6) Reference method EN ISO 8467.

(7) The performance characteristics for individual pesticides are given as an indication. Values for the uncertainty of measurement as low as 30% can be achieved for several pesticides, higher values up to 80% may be allowed for a number of pesticides.

(8) The performance characteristics apply to individual substances, specified at 25% of the parametric value in Table B of Schedule 1.

(9) The performance characteristics apply to individual substances, specified at 50% of the parametric value in Table B of Schedule 1.

(10) The uncertainty of measurement should be estimated at the level of 3 mg/l of the total organic carbon. CEN 1484 Guidelines for the determination of total organic carbon and dissolved organic carbon must be used.

(11) The uncertainty of measurement must be estimated at the level of 1.0 NTU (nephelometric turbidity units) in accordance with EN ISO 7027.

TABLE C

Minimum performance characteristics: trueness, precision and limit of detection- may be used until 31 December 2019

(1) Parameter[(1)]	*(2) Trueness* *(% of parametric value, except for pH)*[(2)]	*(3) Precision* *(% of parametric value, except for pH)*[(3)]	*(4) Limit of detection* *(% of parametric value, except for pH)*[(4)]
Aluminium	10	10	10
Ammonium	10	10	10
Antimony	25	25	25
Arsenic	10	10	10
Benzene	25	25	25
Benzo(a)pyrene	25	25	25
Boron	10	10	10
Bromate	25	25	25
Cadmium	10	10	10
Chloride	10	10	10
Chromium	10	10	10
Colour	10	10	10
Conductivity	10	10	10
Copper	10	10	10
Cyanide[(5)]	10	10	10
1,2-dichloroethane	25	25	10
Fluoride	10	10	10
Hydrogen ion concentration pH (expressed in pH units)[(6)]	0.2	0.2	
Iron	10	10	10
Lead	10	10	10

(1) Parameter[(1)]	*(2) Trueness* *(% of parametric value, except for pH)*[(2)]	*(3) Precision* *(% of parametric value, except for pH)*[(3)]	*(4) Limit of detection* *(% of parametric value, except for pH)*[(4)]
Manganese	10	10	10
Mercury	20	10	20
Nickel	10	10	10
Nitrate	10	10	10
Nitrite	10	10	10
Oxidisability[(7)]	50	25	10
Pesticides[(8)]	25	25	25
Polycyclic aromatic hydrocarbons[(9)]	25	25	25
Selenium	10	10	10
Sodium	10	10	10
Sulphate	10	10	10
Tetrachloroethene[(10)]	25	25	10
Tetrachloromethane	20	20	20
Trichloroethene[(10)]	25	25	10
Trihalomethanes: total[(9)]	25	25	10
Turbidity[(11)]	10	10	10
Turbidity[(12)]	25	25	25

(1) Acrylamide, epichlorohydrin and vinyl chloride to be controlled by product specification.

(2) Trueness is a measure of systematic error, i.e. the difference between the mean value of the large number of repeated measurements and the true value. Further specifications are those set out in ISO 5725.

(3) Precision is a measure of random error and is usually expressed as the standard deviation (within and between batches) of the spread of results from the mean. Acceptable precision is twice the relative standard deviation. This term is further specified in ISO 5725.

(4) Limit of detection is either three times the standard deviation within a batch of a natural sample containing a low concentration of the parameter; or five times the standard deviation of a blank sample (within a batch).

(5) The method determines total cyanide in all forms.

(6) Values for trueness, precision and uncertainty of measurement are expressed in pH units.

(7) Reference method EN ISO 8467.

(8) The performance characteristics for individual pesticides are given as an indication. Values for the uncertainty of measurement as low as 30% can be achieved for several pesticides, higher values up to 80 % may be allowed for a number of pesticides.

(9) The performance characteristics apply to individual substances, specified at 25% of the parametric value in Table B of Schedule 1.

(10) The performance characteristics apply to individual substances, specified at 50% of the parametric value in Table B of Schedule 1.

(11) The performance characteristics apply to prescribed value 4 NTU.

(12) The performance characteristics apply to prescribed value 1 NTU for water leaving surface water treatment works.

PART 3

Monitoring for Indicative Dose and Analytical Performance Characteristics

Monitoring for Compliance with the ID

6. Screening strategy for gross alpha activity and gross beta activity (**1**) may be used to monitor for the parametric indicator value for indicative dose.

If the gross alpha activity is less than 0.1 Bq/l and the gross beta activity is less than 1.0 Bq/l, it may be assumed that the total indicative dose is less than 0.1 mSv and radiological investigation is not needed unless it is known from other sources of information that specific radionuclides are present in water that are liable to cause an excess of 0.1 mSv.

If the gross alpha activity exceeds 0.1Bq/l or the gross beta activity exceeds 1.0Bq/l, analysis for specific radionuclides is required.

The radionuclides to be measured must be based on all relevant information about likely sources of radioactivity.

Calculation of the ID

7. The ID must be calculated from the measured radionuclide concentrations and the dose coefficients laid down in Annex III, Table A of Directive 96/29/Euratom(**2**) or more recent information recognised by the Department, on the basis of the annual intake of water (730l for adults).

Where the following formula is satisfied, it can be assumed that the ID is less than the parametric value of 0.1mSv and no further investigation is required.

$$\sum_{i=1}^{n} \frac{C_i(obs)}{C_i(der)} \leq 1$$

where

$C_i(obs)$ = observed concentration of radionuclide *i*

$C_i(der)$ = derived concentration of radionuclide *i* (see Table D)

n = number of radionuclides detected.

(**1**) Where appropriate gross beta activity may be replaced by residual beta activity after subtraction of the K-40 activity concentration.

(**2**) O.J. No. L159, 29.6.96, P. 27

TABLE D

Derived concentrations for radioactivity in water intended for human consumption

Origin	*Radionuclide*[1]	*Derived concentration (Bq/l)*
Natural	U-238[2]	3.0
	U-234[2]	2.8
	Ra-226	0.5
	Ra-228	0.2
	Pb-210	0.2
	Po-210	0.1
Artificial	C-14	240
	Sr-90	4.9
	Pu-239 / Pu-240	0.6
	Am-241	0.7
	Co-60	40
	Cs-134	7.2
	Cs-137	11
	I-131	6.2

(1) This table includes values for the most common natural and artificial radionuclides; these are precise values, calculated for a dose of 0.1mSV, an annual intake of 730 litres and using the dose coefficients laid down in Annex III, Table A of Directive 96/29/Euratom; derived concentration for other radionuclides can be calculated on the same basis, and values can be updated on the basis of more recent information recognised by the Department.

(2) This allows only for the radiological properties of uranium, not for its chemical toxicity.

Performance characteristics and method of analysis.

8. For the following parameters and radionuclides, the method of analysis used must, as a minimum be capable of measuring activity concentrations with a limit of detection specified below in Table E:

TABLE E

Parameters and radiouclides	*Limit of detection*[1][2]
Tritium	10 Bg/l[3]
Radon	10 Bg/l[3]
gross alpha activity	0.04 Bg/l[4]
gross beta activity	0.4 Bg/l[4]
U-238	0.02 Bg/l
U-234	0.02 Bg/l

Parameters and radiouclides	*Limit of detection*[(1)(2)]
Ra-226	0.04 Bg/l
Ra-228	0.02 Bg/l[(5)]
Pb-210	0.02 Bg/l
Po-210	0.01 Bg/l
C-14	20 Bg/l
Sr-90	0.4 Bg/l
Pu-239/Pu-240	0.04 Bg/l
Am-241	0.06 Bg/l
Co-60	0.5 Bg/l
Cs-134	0.5 Bg/l
Cs-137	0.5 Bg/l
I-131	0.5 Bg/l

(1) The limit of detection must be calculated according to the ISO standard 11929:2010 entitled "Determination of the characteristic limits (decision threshold, detection limit and limits of the confidence interval) for measurements of ionising radiation - Fundamentals and application", with probabilities of errors of 1st and 2nd kind of 0.05 each.

(2) Measurement uncertainties must be calculated and reported as complete standard uncertainties, or as expanded standard uncertainties with an expansion factor of 1.96, according to the ISO IEC Guide 98-3:2008 entitled "Guide to the expression of uncertainty in measurement".

(3) The limit of detection for tritium and for radon is 10% of the corresponding parametric value of 100 Bg/l.

(4) The limit of detection for gross alpha activity and gross beta activities is 40% of the screening values of 0.1 Bq/l and 1.0 Bq/l respectively.

(5) This limit of detection applies only to initial screening for indicative dose for a new water source. If initial checking indicates that it is unlikely that Ra-228 exceeds 20% of the derived concentration, the limit of detection may be increased to 0.08 Bq/l for routine Ra-228 nuclide specific measurements, until a subsequent re-check is required.