

Refinery effluent analysis methodologies for relevant parameters from EU - regulatory regimes



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Prepared under supervision of the Refinery Water Management Task force STF/34, of the CONCAWE Water, Soil and Waste Management Group (WSWMG) by:

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## ABSTRACT

This report provides guidance to CONCAWE members on the analytical methods that might be used to monitor oil refinery effluents for those refinery-specific parameters covered by relevant European legislation and a comparison of the methods that are used today, as reported in the last Effluent Survey.

A method assessment programme is presented whereby the performance of methods of analysis (used to monitor oil refinery effluents) can be compared and prioritised in order of their analytical performance capabilities. Methods for a specific parameter, which is clearly and unambiguously defined, are compared with each other and then prioritised in terms of their overall quality. The quality of these methods is based on an assessment of a combination of characteristic features, namely, precision, bias or recovery, limit of detection (where appropriate), indicative costs, and ease of use. Ranking scores for each feature are assigned to various ranges of each feature, and then added together to give an overall ranking value. The method exhibiting the lowest overall ranking value is deemed the most appropriate method for analysing that parameter.

Within this report, several recommendations are made in terms of comparing results of analyses or their associated uses. Where data are to be compared for a particular parameter, then, all CONCAWE members involved in this comparison should agree common objectives, in advance. These include defining a common definition for the:

- i) Parameter being analysed and compared;
- ii) Limit of detection, and how this concentration value should be calculated;
- iii) Limit of quantification, and how this concentration value should be calculated and how it is to be applied for selective reporting purposes; and
- iv) Uncertainty of measurement and how it should be calculated.

It is further recommended these involved members should agree on the range of values and ranking scores chosen to reflect the performance characteristic features used in the method assessment programme, or establish and agree alternative values.

In addition, CONCAWE members should agree to provide details of the methods they use and the performance data obtained on their own specific effluents, so that appropriate and realistic method assessment comparisons can be undertaken. CONCAWE desires to collate this appropriate information relevant to their specific sector from its members in a way that the assessment programme can be regularly updated with new data, enabling methods to be compared in a way that is more directly applicable to the refinery sector.

## **KEYWORDS**

Method comparisons and assessments, performance characteristics (precision, bias, recovery, limit of detection, limit of quantification, uncertainty of measurement)

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# SUMMARY

This CONCAWE-commissioned report has been developed to inform the Refining Industry, Regulators and Consultants as to the modern chemical analytical methods currently utilised in support of EU legislative and regulatory obligations. The report includes a compilation of available analytical methods for routine and non-routine refinery effluent quality monitoring and provides a basis for their comparative assessment to fulfil all the legislative requirements at an EU-level, as well as, specific Members State's requirements.

In recent years CONCAWE members, who operate 115 refinery installations in Europe have provided details of these methodologies. This report has determined a degree of variation in the deployment of analytical methods and an associated variability of the reported limits of detection (LoD) and limits of quantification (LoQ) values for these methods for the parameters analysed. In the most extreme case for one single parameter, 39 different analytical methods are in use today with a distribution of LoQs that vary by four orders of magnitude.

The report establishes a basis for the objective comparison of methods deployed. In the first instance the report finds that before method performance parameters can be compared, the parameter of interest itself needs to be clearly and unambiguously defined to ensure that there is no confusion as to the specific analyte that is being analysed. This is illustrated by an example of metal analysis where these potential problems surface with differences between soluble forms, metal particulates and total metal. Similar reasoning has been applied, for example to the measurement of phenols, TPHs, PAHs and toxic metals.

Once agreement is reached as to the precise definition of the parameter to be analysed, the capability of available analytical methods can be compared on the basis of a method's performance characteristics. Where an appropriate validation process and performance data are available, the report assesses the importance of method performance characteristics including a method's precision, bias or recovery, limit of detection (where appropriate), indicative cost and ease of use.

The methods for 53 refining industry relevant parameters, most of which are prescribed in the various legislative frameworks, have been assessed in terms of their applicability, quality and analytical performance. The result of this assessment is an overall ranking of methods based on a selection of performance characteristics that can be used as an effective like for like comparison of one method to another for judging its suitability.

The report offers an opinion on the statistical interpretation of results which for each parameter analysed relates to a critical level of interest. This may correspond to an Environmental Quality Standard (EQS) value, a maximum or periodic average permit concentration agreed under a permit condition or an operator self-imposed level that is being used to measure whether a refining process is under operational control.

In addition the report goes on to determine whether a method can satisfy (in terms of its limit of quantification and uncertainty of measurement) the appropriate EQS value for those parameters where an EQS has been prescribed.

A basic 'assessment tool' has also been developed that allows for the entry of new methods or those that have not been previously documented at a local level. This

allows a user to enter the associated characteristics of a method for an objective comparison against the existing set of methods that have already been identified for a given parameter.

The report concludes with the intention of CONCAWE to extend the collation of parameter and analytical method information relevant to the refinery sector, allowing for a continual assessment of available methods in the future with the tool developed in this project and advising the CONCAWE Membership on the applicability of these methods.

# 1. INTRODUCTION

During the preparation of the CONCAWE input on the revision of the Best Available Techniques (BAT) reference document (BREF) for the refining industry [1], a data evaluation of the last refinery effluent survey was performed. This survey, that took place in 2012, contains information provided by over 100 CONCAWE membership refineries, covering the years 2004 and 2005. The evaluation of the information obtained in this or earlier survey has been published in CONCAWE reports 2/10 [2] 2/11 [3] and 6/12 [4].

One of the most striking (but not unexpected) observations from this evaluation was the variation of the analytical methods applied, and the associated variability of the reported limit of detection (LoD) or limit of quantification (LoQ) values for these methods when applied to a particular parameter, i.e. specific analyte, substance or groups of substances being analysed or determined. For one particular parameter, 39 different analytical methods were reported to be applied and the distribution of LoQs was reported to vary by four orders of magnitude, with some of these being higher than the BREF proposed best available technique associated emission level (BATAEL). Comparing methods and associated performance data with this degree of variability in the analytical methods applied to individual parameters presents some challenges and requires caution in drawing conclusions, especially in cases where the parameter is not clearly and unambiguously defined.

In addition, the European Commission adopted a directive (2009/90/EC) in 2009 (often referred to as the QA/QC directive) that lays down technical specifications for chemical analysis and monitoring of water status [5] under the Water Framework Directive (WFD, 2006/60/EC) [6] and associated legislation such as the Directive on Environmental Quality Standards (EQSs, 2008/105/EC) [7]. The QA/QC directive establishes minimum performance criteria for LoQ and uncertainty of measurement (UoM) for methods of analysis to be applied by member states when monitoring water status, sediment and biota, as well as requirements for demonstrating the quality of analytical results.

Although not directed at effluent monitoring, the principles included in this Directive also may offer guidance to assure that there will be a level playing field. Therefore, CONCAWE believes that similar performance criteria that take into account the purpose of the analysis may become applicable to industries reporting to any "competent authority" that require effluent quality data under the WFD, the Industrial Emissions Directive (IED, 2010/75/EU), formerly known as the IPPC Directive [8], and the European Pollutant Release and Transfer Register Regulations (EPRTR, EC/166/2006) [9]. CONCAWE is therefore of the opinion that the oil refining industry could benefit from CONCAWE-supported guidance on analytical methods that can fulfil these requirements for establishing the chemical quality of oil refinery effluents prior to discharge and dilution, into receiving waters in the environment.

This report provides this guidance and identifies those analytical methods available for the monitoring of effluents for refinery-specific parameters, i.e. those analytes relevant to oil refineries, and that are listed in the aforementioned legislation. In addition, other analytes or parameters that might also be relevant to the oil industry are considered as well. A partnership between Beta Technology Ltd and the UK's Environment Agency's National Laboratory Service was commissioned by CONCAWE to undertake a comparison of

- i) The methods of analysis used by oil refinery process operators operating within Europe; and
- ii) The parameters analysed by these operators.

This comparison exercise was to include a brief review of the literature to ascertain if other methods could be used in addition to those cited by CONCAWE members in their response to the 2010 Effluent Quality Survey that was performed in 2011 [4] for parameters, i.e. specific substances, compounds or group of compounds, reported in the survey.

This exercise was also to investigate whether the methods used were appropriate and fit-for-purpose, and were of sufficient quality to satisfy the requirements of the QA/QC Directive (2009/90/EC) [5]. In addition, the exercise was to investigate the parameters analysed, and to ascertain whether a consistent approach was being adopted by oil refinery operators across Europe or whether specific circumstances at individual operator sites prevailed, resulting in a more selective approach being chosen for the analyses carried out.

Information provided by CONCAWE in the form of a spread sheet was used as the basis for the comparison of the methods used and parameters analysed. A total of 23 countries provided data to CONCAWE in a survey conducted in 2011 [4]. These data included details of the analysis of a total of 61 parameters and a huge variety of methods used to determine these parameters (see **Table 1**). Whilst information was provided on these 61 parameters and associated methods, no performance data were included, as this information was not requested.

Table	1
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Parameters reported in the 2010 CONCAWE effluent survey\*

	Parameter	Number of responses / effluents (Number of countries)	Responses with sufficient detail provided	Number of different methods cited	Legislative framework
1	Aluminium	2 / (2)	-2	2	No specific reference
2	Ammonia	51 / (15)	38	17	No specific reference
3	Ammoniacal nitrogen	62 / (22)	44	23	No specific reference
4	Anthracene	46 / (14)	27	19	WFD, EPRTR
5	AOX	3 / (1)	1	1	IED, EPRTR
6	Arsenic	94 / (19)	63	21	WFD, IED,EPRTR
7	Benzene	57 / (15)	24	28	WFD, EPRTR
8	benzo[b]fluoranthene	28 / (15)	21	17	WFD, EPRTR
9	benzo[k]fluoranthene	27 / (10)	21	10	WFD, EPRTR
10	benzo[ <i>g</i> , <i>h</i> , <i>i</i> ]perylene	113 / (14)	60	16	WFD, EPRTR
11	benzo[a]pyrene	78 / (14)	22	17	WFD, EPRTR
12	BOD	109 / (23)	88	20	WFD, IED
13	BTEX	2 / (2)	1	1	EPRTR
14	Cadmium	71 / (20)	45	18	WFD, EPRTR
15	chloride	78 / (18)	55	21	EPRTR
16	Chromium	107 / (20)	70	21	EPRTR
17	Chromium (VI)	37 / (12)	26	11	No specific reference

	Parameter	Number of responses / effluents	Responses with sufficient	Number of different	Legislative framework
		(Number of	detail	methods	
10	O sh sh	countries)	provided	cited	
18	Cobalt	37 / (14)	19	7	IED, REF-BREF
19	COD	136 / (23)	111	20	WFD, IED
20	Copper	157 / (20)	145	22	EPRTR
21	dichloromethane	28 / (11)	11	11	WFD, EPRTR
22	ethylbenzene	75 / (14)	46	22	EPRTR
23	extractable substances with petroleum ether	1 / (1)	1	1	No specific reference
24	fluoranthene	81 / (16)	55	17	WFD, EPRTR
25	fluoride	64 / (13)	46	14	EPRTR
26	free cyanide**	77 / (16)	50	15	EPRTR
27	indeno[1,2,3-cd]pyrene	74 / (14)	52	17	WFD, EPRTR
28	iron	53 / (13)	32	18	No specific reference
29	Kjeldahl nitrogen	38 / (10)	24	10	No specific reference
30	Lead	73 / (20)	46	20	WFD, EPRTR, IED
31	Manganese	1 / (1)	1	1	No specific reference
32	Mercury	64 /(19)	40	17	WFD, EPRTR, IED
33	MTBE	39 / (11)	18	13	No specific reference
34	MTBE + ETBE	1 / (1)	1	-	No specific reference
35	naphthalene	46 / (14)	25	13	WFD, EPRTR
36	Nickel	70 / (18)	40	19	IED, EPRTR
37	nitrate	66 / (17)	49	19	WFD, IED,
38	nitrite	59 / (15)	40	17	IED
39	OiW or TPHs	91 / (23)	52	21	IED
40	PAH	1 / (1)	1	1	WFD, EPRTR
41	pentachlorbenzene	17 / (8)	7	5	WFD, EPRTR
42	рН	120 / 21	63	15	No specific reference
43	phenols	79 / (23)	54	21	IED, EPRTR
44	phosphate	1 / (1)	1	1	WFD, IED
45	Selenium	31 / (10)	20	10	No specific reference
46	sulphate	1 / (1)	1	-	No specific reference
47	suphide	78 /(19)	48	19	No specific reference
48	suphide / mercaptan (sum)	1 / (1)	1	-	No specific reference
49	suphite	15 / (9)	10	8	No specific reference
50	temperature	84 /(19)	12	4	No specific reference
51	tetrachloroethylene	1 / (1)	1	-	EPRTR, EQSD
52	TOC	64 / (15)	35	8	IED, EPRTR
53	Toluene	83 / (15)	54	24	EPRTR
54	total nitrogen	99 /(20)	40	20	EPRTR
55	total phosphorus	103 /(23)	26	22	EPRTR
56	total suspended solids	123 / (22)	20	19	IED
57	toxic metals	1 / (1)	1	-	No specific reference
58	trichloromethane	40 / (11)	21	11	WFD, EPRTR
59	Vanadium	50 / (15)	31	12	No specific reference
60	xylenes	87 / (15)	57	26	EPRTR
	Zinc	100 / (20)	66	19	EPRTR

The full results of this survey will be published in due course. Part of the survey is already published [11]. "EPRTR refers to cyanide as "cyanides (as total cyanide)" and "hydrogen cyanide".

For each parameter, numerous methods were cited by oil refinery operators. In the majority of situations, a published reference was provided as the source of each method where, following further investigation, additional details have been obtained. These methods are listed in **Appendix 1**. Where other methods, that could also have been used but which were not cited in the CONCAWE survey, have been identified, these methods are also shown in **Appendix 1**, and are presented in italic, red font.

In other cases, no information was provided or only limited information was given on the method. In all of these cases, the information was insufficient to classify the method or provide a source of the method and these methods are marked "NIA" in **Appendix 1**. Where necessary these methods might provide additional information if investigated further.

Whilst a study of the methods cited in the 2010 CONCAWE survey has been undertaken, some degree of caution should be exercised as:

- (i) Where a cited reference has been given in the survey, it is not clear whether the method has been used as published, or whether the method was used as the basis of the procedure (and the procedures in the original publication were adapted in some way to reflect the specific nature of the oil refinery effluent analysed).
- (ii) It is not clear how relevant the cited methods are in relation to the oil refinery effluents analysed. For example many of the cited references are applicable to drinking waters, ground and river waters, and municipal waste effluents, and not specifically to oil refinery effluents.
- (iii) No information has been provided to indicate whether each oil refinery operator has properly validated the procedures used at its own site, or has simply used the cited reference as the source method or the basis of the method.
- (iv) For some analyses from a single operator there are several methods cited for a particular parameter. Thus, it may be the case, that procedures have been developed or adopted, based on a combination of reported determinations. No specific information on these conditions has been provided, nor performance data reported.

#### 1.1. COMPLIANCE MONITORING VERSUS OPERATIONAL MONITORING

Compliance monitoring is monitoring whereby specific analyses or determinations are carried out according to specified requirements prescribed in legislation and enforced by regulators, or operating permits granted by "competent authorities". This normally entails defined sampling frequencies where samples are taken for the analysis of specific determinations or parameters. These analyses are generally undertaken to ascertain if contaminants are present in the samples taken and whether their concentrations are above or below those defined in the legislation or in operating permits, for those parameters analysed. Where these levels exceed those defined, this can facilitate the consideration of potential remedial action in order to reduce the levels prior to these contaminants being discharged into the environment. Alternatively, the results can be used for other purposes (for example in the determination of load, i.e. the amount of parameter being released into the environment over a specified period of time).

Operational monitoring, however, is usually carried out on a more flexible basis, generally at the discretion of the operator rather than the regulator or permitting authority, to ascertain if process conditions at a particular site are under proper control, and operations are operating satisfactory or correctly. Specific analyses need not necessarily be carried out, but rather surrogate analyses can be used as alternatives to specific determinations. For example, the determination of TOC may be undertaken to provide a measure of organic pollution within a sample. It will not, however, identify the actual pollutant or give a true estimate of the actual pollutant concentration. In this context, TOC measurements can usefully be used to determine or monitor trends in organic contamination levels.

Also, the determination of substances soluble in a particular organic solvent may give an indication of organic contamination such as TPHs. This determination will not however give a true measure of TPH levels as other organic substances (either polluting or non-polluting) may also be extracted. Again, this determination is a useful surrogate analysis for ascertaining trends of organic levels in samples, whether regarded as contaminating or not. In addition, the determination of groups of compounds, typical of an operator's installation, can give a measure of the performance of the installation or the waste water treatment process. Examples include the determination of such groups as TPHs, BTEX and PAHs. In the case of BTEX, these determinations can provide an indicative measure of the total level of hydrocarbon present. Similarly, TPH determinations (CONCAWE reports 96/52 [10], 3/10 [11] and 6/12 [4]) can be carried out to provide an indication of trends in organic levels in samples, and also the performance of operator's installations.

Compliance monitoring is usually carried out employing strictly defined quality assurance systems including proper validation of fit-for-purpose methods, analyses of quality control samples, and standard solutions or certified reference materials etc. Whilst operational monitoring may be carried out under these strictly defined conditions, it need not necessarily be so. The conditions used for operational monitoring can be less demanding and may seem less challenging from those used for compliance monitoring. Where possible and appropriate, compliance monitoring and operational monitoring may be combined for economic reasons in order to conserve resources.

A distinction should therefore be made when an operator undertakes analytical monitoring. This is to ascertain whether the monitoring is carried out for compliance purposes or for operational reasons. In addition, whilst information gained from compliance monitoring may also be used for operational purposes, data from operational monitoring may not be appropriate for compliance purposes, unless it has been demonstrated that they have been generated under the same strict conditions applicable to and prescribed for compliance monitoring, and also that the parameter monitored for operational needs is relevant to compliance purposes, there would be little merit analysing TOC levels for operational monitoring, irrespective of the quality of this analysis and submitting these TOC results instead of TPH results.

## 2. LEGISLATIVE FRAMEWORK

The discharge of oil refinery effluents into the environment is subject to regulation according to national legislation that is transposed from European legislation incorporating the requirements of European directives into nation regulation. Whilst the requirements of European directives often specify minimum standards and a common framework within which to operate, individual national legislation based on European directives may require a more stringent approach to be adopted, specifying more exacting standards and requirements. These approaches are usually prescribed at the discretion of individual nations, reflecting their own individual national concerns.

The more important pieces of European legislation concerning the discharge of effluents to the aqueous environment include:

- i) Directive 91/271/EEC of 21 May 1991 concerning urban waste water treatment [26].
- ii) Directive 2000/60/EC of the European parliament and of the council of 23 October 2000 establishing a framework for Community action in the field of water policy, commonly referred to as the Water Framework Directive [5].
- iii) Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions [7].
- iv) Directive 2008/56/EC of the European parliament and of the council of 17 June 2008 establishing a framework for community action in the field of marine environmental policy, commonly referred to as the Marine Strategy Framework Directive [27].
- v) Directive 2008/105/EC of the European parliament and of the council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing council directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending directive 2000/60/EC of the European parliament and of the council [29].
- vi) Regulation (EC) No 166/2006 of the European parliament and of the council of 18 January 2006 concerning the establishment of a European Pollutant Release and Transfer Register (and amending Council Directives 91/689/EEC and 96/61/EC) [8].
- vii) Directive 2009/90/EC of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European parliament and of the council, technical specifications for chemical analysis and monitoring of water status, commonly referred to as the QA/QC directive [5].
- viii) Directive 2006/11/EC of the European parliament and of the council of 15 February 2006 on pollution caused by certain dangerous substances discharged into the aquatic environment of the community [28].

In addition, individual national requirements may also need to be taken into account. Within the UK there is the Environment Agency's Monitoring Certification Scheme (MCERTS) prescribing performance criteria for analyses involving water monitoring.

For example, the Performance Standard for Organisations undertaking Sampling and Chemical Testing of Water - Part 1 - Sampling and chemical testing of untreated sewage, treated sewage effluents and trade effluents. (See www.mcerts.com). Some of the requirements contained within this performance standard are more stringent than corresponding requirements contained in directive 2009/90/EC. The requirements of individual national legislation would of course not need to be adopted or satisfied in other countries.

## 2.1. LEGISLATIVE REQUIREMENTS

Methods of analysis used for the regulatory monitoring of the aquatic environment as described in Directives 2000/60/EC and 2008/105/EC should meet the minimum performance criteria prescribed in Directive 2009/90/EC [5]. This includes establishing an uncertainty of measurement (UoM) of 50% or below based on the relevant EQS [5]) and a limit of quantification (LoQ) equal to or below a value of 30% of the relevant EQS [5]). In cases where no EQS value is prescribed or in the absence of a method of analysis meeting the minimum performance criteria, then monitoring should be carried out using best available techniques not entailing excessive costs (BATNEEC).

Thus, it may be inferred that for parameters where no EQS value is defined, the requirements for performance criteria LoQ and UoM need not be applicable. This provision raises issues of what constitutes BATNEEC, as neither excessive costs are defined in the legislation, nor are criteria presented for assessing the best available techniques. In addition, where a method of analysis for a particular parameter does not meet the performance criteria requirements, this raises the issue of whether another technique should be used in place of the method that doesn't satisfy the performance criteria, provided the technique is shown to be the best available not entailing excessive costs.

In terms of their calculation, the performance characteristics LoQ and UoM are not clearly and unambiguously defined in the QA/QC Directive [5]. See also sections 5.4, 5.5 and 5.6. Whilst the LoQ should be determined to a commonly agreed definition, the directive fails to state what this definition should be, and also the organisations that should agree to it. Without clarification, this effectively inhibits the enforcement of this legislation, and hinders a single, consistent approach being adopted across Europe.

Where a mean value needs to be calculated, for example determining the annual mean value of a series of concentrations obtained over a one-year period, then if a concentration is reported to be below a minimum reporting value, i.e. the LoQ, then one-half of the LoQ concentration should be used in the calculation of the mean value [5]. Where the calculated mean is less than the LoQ concentration, then the mean value should be reported as "less than limit of quantification". Where a determination involves summing the concentrations of two or more individual substances and the concentration of an individual substance is below the LoQ then the concentration of the individual substance should be set to zero and not one-half of the limit of quantification concentration [5].

Where there are no methods which comply with the minimum performance criteria, monitoring should be based on BATNEEC. Since the quality of these techniques, in terms of their performance, may be questionable, the analyses should be supported by on-going quality assurance and quality control procedures to demonstrate their suitability. The QA/QC Directive states that technical operations, to ensure the quality and comparability of analytical results, should follow quality management system practices, for example those described in ISO 17025 [12]. Also, that laboratories performing chemical analysis should demonstrate their competences through the participation in internationally or nationally recognised proficiency testing programmes and through the use of available reference materials

It is the responsibility of a national government to transpose relevant directives, including the Industrial Emissions Directive (2010/75/EU) into its own national legislation and then, usually, for national "competent authorities" to enforce this legislation and ensure it is applied correctly.

Usually, a system of granting permits is devised whereby operators are allowed (granted permission) to discharge their effluents into the environment provided the discharges meet the conditions specified in the permit. Within these permits conditions are agreed between the competent authority and the operator where specific parameters (depending on the nature of the discharged effluent) are routinely monitored over a specified period of time. When concentrations of these parameters are below agreed levels, the discharge is deemed compliant within the permit conditions. If they are not, remedial action may need to be undertaken. Conditions within the permit may also include the use of specific methods of analysis for specific parameters. The competent authority and the permit holder agree the analyses to be performed and the frequency of sampling, and the competent authority may impose other conditions, when deemed appropriate, and in response to specific local circumstances. These conditions may be quite separate and different to the requirements of the directives. Periodically, the operator provides this monitoring data to the competent authority.

The competent authority collates data from all its operators and other information as necessary, such as discharge and river flow rates, etc. and then submits this evidence, on behalf of the member state, to the EU as part of its responsibility under the requirements of the directives. The member state is thus responsible for ensuring the requirements of the directives are satisfied.

To date, 33 substances have been allocated specific EQS values [6]. Those of relevance to oil refinery process operators and their effluent analyses are shown in **Table 2**. Also included in this table are the maximum UoM and LoQ values, based on the annual average EQS values of these parameters. Only those methods that satisfy these UoM and LoQ requirements of the directive [5] should be used to monitor these parameters, where samples are taken in accordance with the WFD.

Table 2	Environmental Quality Standards for substances relevant to oil refineries and
	the associated minimum analytical method performance limits

Parameter	<b>AA-EQS</b> <sup>(1,2)</sup>	<b>UoM</b> <sup>(1,2,3)</sup>	<b>LoQ</b> <sup>(1,2,3)</sup>	MAC-EQS <sup>(1,2)</sup>
	µg/l	µg/l	µg/l	µg∕l
Anthracene	0.1	0.05	0.03	0.1
Benzene	10	5	3	50
Benzo[ <i>b</i> ]fluoranthene <sup>*</sup>	0.00017	0.000085	0.000051	0.017
Benzo[k]fluoranthene*	0.00017	0.000085	0.000051	0.017
Benzo[ <i>g,h,i</i> ]perylene <sup>*</sup>	0.00017	0.000085	0.000051	0.0082
Benzo[ <i>a</i> ]pyrene <sup>*</sup>	0.00017	0.000085	0.000051	0.27
Cadmium <sup>(5)</sup>	0.25	0.125	0.075	1.5
Dichloromethane	20	10	6	n.a. <sup>(4)</sup>
Fluoranthene <sup>*</sup>	0.0063	0.00315	0.00189	0.12
Indeno[ <i>1,2,3-cd</i> ]pyrene <sup>*</sup>	0.00017	0.000085	0.000051	n.a. <sup>(4)</sup>
Lead <sup>*</sup>	1.2	0.6	0.36	14
Mercury <sup>*</sup>	na <sup>(4)</sup>	-	-	0.07
Naphthalene	2.0	1.0	0.6	130
Nickel <sup>*</sup>	4.0	2.0	1.2	34
Pentachlorobenzene	0.007	0.0035	0.00021	n.a. <sup>(5)</sup>
Trichloromethane	2.5	1.25	0.75	n.a. <sup>(5)</sup>

Notes

(1) Values are for fresh inland surface waters

(2) As prescribed in directive  $2008/105/EC^{(7)}$ .

(3) Based on requirements contained in directive 2009/90/EC<sup>(5)</sup> for the AA-EQS value.

(4) n.a. indicates not applicable.

(5) Value depends on the hardness of the water; the harder the water the higher the EQS. The highest EQSs of 5 values are quoted.

Taken from Analytical Methods [13] for the new proposed Priority Substances of the European Water Framework Directive (WFD), Robert Loos, European Commission - DG Joint Research Centre (JRC) Institute for Environment and Sustainability (IES) Water Resources Unit (H01) Ispra, Italy.

## 3. MEANINGFUL COMPARISON OF PARAMETERS

For any meaningful comparison to be undertaken, it must be ensured that the comparison is carried out on a "like-for-like" basis. Thus, in the first instance, it should be established whether all participants within the exercise measured exactly the same parameter, and if this parameter is defined in exactly the same way by each of them. This means that the parameter should be clearly and unambiguously defined. Where this is the case, it may, depending on the results subsequently obtained, be immaterial which method is used. Where the definition of the parameter is not clear, or is ambiguous, the procedures used within any method may dictate the result that is generated. Even when parameters apparently seem to be defined clearly, for example, lead, the method used should adequately distinguish whether it determines:

- i) Lead in solution, i.e. soluble lead,
- ii) Lead adsorbed onto solid material present in solution, i.e. particulate lead,
- iii) Total lead, comprising combination of i) and ii) above.

Without this understanding, there would be little point conducting a comparison exercise of method performances and laboratory and analyst capabilities unless identical parameters are being determined and compared. For instance, in the above example, there would be little point comparing methods that determine only the soluble lead fraction of a sample with methods that determine say the particulate lead content of the sample or a combination of particulate lead and soluble lead fractions, as different fractions are being determined, even though they are classified as lead. Thus, it must be ensured that a method for determining soluble lead is compared only with other soluble lead methods. Similar reasoning applies to all parameters and especially to determinations involving, for example, measurements for phenols, TPHs, PAHs, toxic metals, etc. See also section 9.3.

Where a comparison of data obtained for a particular parameter is carried out either by a competent authority or by operators representing a specific industrial sector, all parties should agree a common definition of the parameter being analysed and compared.

For example, if concentrations of phenols are to be compared, then the precise number and identity of the individual phenols being analysed and compared should be agreed See section 9.3.2. Likewise, if the load of TPHs, i.e. the amount of petroleum hydrocarbons being released into the environment is to be compared, the definition of TPH should be agreed. This might include defining the same range of hydrocarbons both aliphatic and aromatic. Similarly, a sampling and sample treatment procedure may also need to be agreed. See section 9.3.4.

In addition, where a parameter seems to be clearly and unambiguously defined, for example easily liberated cyanide (see section 9.3.6) caution should be exercised in the assessment and comparison of methods for this kind of parameter. For these parameters, the conditions of the analysis, for example the pH of the extraction, define the result that is generated. Thus changing these conditions may change the result obtained. Methods of this type should be treated as if the parameter is not clearly defined. Similar reasoning applies to parameters like COD, sulphide, BOD etc.

# 4. SAMPLING

For waters and effluents, the European technical committee responsible for producing standards, namely CEN TC 230 - Water Analysis, has agreed that the development of standards concerning sampling should be undertaken within the corresponding international technical committee, namely ISO TC 147 - Water Quality, and not within Europe. Under this agreement, numerous standards have now been developed within the ISO 5667 series. To date, ISO 5667 consists of the following parts<sup>1</sup>;

- Part 1: Guidance on the design of sampling programmes and sampling techniques
- Part 3: Guidance on the preservation and handling of water samples
- Part 4: Guidance on sampling from lakes, natural and man-made
- Part 5: Guidance on sampling of drinking water from treatment works and piped distribution systems
- Part 6: Guidance on sampling of rivers and streams
- Part 7: Guidance on sampling of water and steam in boiler plants
- Part 8: Guidance on the sampling of wet deposition
- Part 9: Guidance on sampling from marine waters
- Part 10: Guidance on sampling of waste waters
- Part 11: Guidance on sampling of ground waters
- Part 12: Guidance on sampling of bottom sediments
- Part 13: Guidance on sampling of sludges from sewage and water treatment works
- Part 14: Guidance on quality assurance of environmental water sampling and handling
- Part 15: Guidance on preservation and handling of sludge and sediment samples
- Part 16: Guidance on bio-testing of samples
- Part 17: Guidance on sampling of suspended sediments
- Part 18: Guidance on sampling of groundwater at contaminated sites
- Part 19: Guidance on sampling of marine sediments

<sup>&</sup>lt;sup>1</sup> The detail of Part 2 has been subsumed into Part 1 in a recent revision of Parts 1 and 2

- Part 20: Guidance on the use of sampling data for decision making Compliance with thresholds and classification systems
- Part 21: Guidance on sampling of drinking water distributed by tankers or means other than distribution pipes
- Part 22: Guidance on design and installation of groundwater sample points
- Part 23: Determination of significant pollutants in surface waters using passive sampling

Not all of these parts are directly applicable to the sampling of oil refinery effluents, but generally, all contain some useful information and many of the procedures described can be adapted to suit situations relevant to oil refinery effluents. Parts 1, 3 and 10 are of particular relevance to oil refinery effluents.

Another useful document giving advice and guidance on the sampling of waters is that published within the MEWAM series [14]. In addition to providing advice on sampling this document also describes techniques for calculating the amount of a specific parameter released into the environment. This amount is usually referred to as the load, and is often expressed as the mass of parameter released into the environment over a period of time, usually based on the concentration of the parameter in the effluent, and the flow-rate of the effluent. In situations where a minimum reporting value is used and the concentration of the parameter is reported as being below this limit of quantification, the load cannot be calculated with confidence, and only a potential estimate can be provided. If a minimum reporting value is not used, then the load can only be calculated using concentrations that are determined and found to be above the limit of detection. If the concentration is below the LoD concentration, i.e. the concentration cannot be determined with any degree of confidence, a potential estimate of the load can only be provided. See also section 6.

General procedures for a more statistical approach to sampling can be found in Measurement uncertainty arising from sampling - a guide to methods and approaches [15], and Uncertainty from Sampling [16].

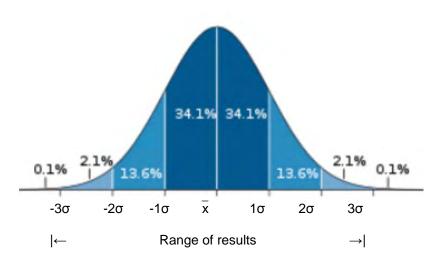
In addition, sampling procedures are often provided along with the analytical details described for determining parameters of interest, for example many of the international standards written for the analysis of specific parameters. Details of these procedures tend however, to be more general than specific and relate to nonoil refinery effluent matrices, and may not be entirely relevant to oil refinery operators. In these documents advice and guidance is also given for specific parameters on the type of sample containers to use, the conditions under which and the time period for which samples may be stored before analysis, the amount of sample to be collected and whether stabilisation or preservation of the sample should be required.

## 5. PERFORMANCE CHARACTERISTICS

In order to assess the capability of a method's performance certain features need to be known. These features, commonly referred to as performance characteristics, include such terms as precision, bias, recovery, limit of detection, limit of quantification, etc. Without an understanding and estimation of the values of these characteristics, it is impossible to judge whether results generated by the methods are suitable and fit for their intended purpose. Values for these characteristics can only be established via the undertaking of a proper validation process, which must be carried out before samples can be analysed routinely and results reported, so that analysts (and others) can have confidence in the results generated following validation. See also section 5.7

### 5.1. PRECISION

When an analysis is carried out many times, the results obtained are expected to be spread over a range of values. This range is often called a Gaussian (or normal) distribution. See **Figure 1**.



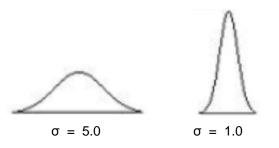
#### *Figure 1* Gaussian distribution

Approximately 68% of results lie within  $\pm 1$  standard deviation, i.e.  $\pm 1\sigma$ Approximately 95% of results lie within  $\pm 2$  standard deviations, i.e.  $\pm 2\sigma$ Approximately 99.7% of results lie within  $\pm 3$  standard deviations, i.e.  $\pm 3\sigma$ 

The average value of all the replicated results is called the mean,  $\bar{x}$  (referred to as x-bar) and is calculated as the sum of all the replicated results divided by the total number of results. The precision of an analytical method is an expression of how close replicated results are to each other. It is a measure of the range of these results, from the highest to the lowest value, and there are several ways in which precision can be expressed. These include the standard deviation,  $\sigma$ , relative standard deviation, RSD, and standard deviation (or error) of the mean, SDM. Where the standard deviation is not based on the whole population of results, the term s is used. See **Appendix 2**. Thus, depending on how it is calculated, precision can be expressed in either the same units as the result (for example  $\mu$ g/l) or as a fraction or percentage term.

As precision increases, i.e. is deemed to improve and get better, then the precision value decreases, and the shape of the Gaussian distribution becomes less "bell-shaped" and more compressed. See **Figure 2**.

*Figure 2* Dependency of the Gaussian distribution on standard deviation

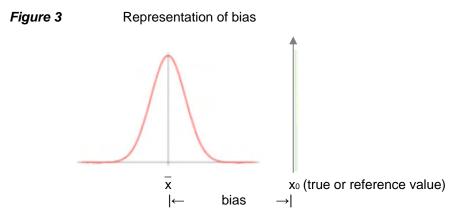


The lower the precision value, i.e. as precision increases then more confidence can be expressed in the results generated. Generally, precision represents random variations within the analytical determination. For example, the small variations observed when repeatedly dispensing the same volumes of solutions or weighing the same quantities of solid. This might occur for instance when 5.00 ml of solution needs to be repeatedly pipetted and 4.95, 5.01, 5.03, 4.89, 4.99, 5.05, 5.03 and 5.01 ml quantities are actually dispensed.

For many methods, it is shown that the performance data for precision values generated for a particular method vary with the concentration levels being determined. This generally reflects the difficulties encountered when low concentrations are determined, compared to higher concentrations. This variation however cannot be predicted. For example, for some methods, as the concentration levels increase, the precision also increases. For other methods, when the concentration levels increase, the precision is shown to decease. Only by generating performance data for each method can the relationship between precision and concentration be demonstrated. A similar situation arises with bias and recovery and the concentration levels being determined.

### 5.2. BIAS

As with precision, when an analysis is carried out many times, the results obtained usually follow a Gaussian distribution where the average value of all the replicated results is called the mean,  $\bar{x}$ . The bias of a method is a measure of the mean of replicated results generated by the analysis of a sample and how close this result is to the actual true result or stated certified reference value. See **Figure 3**.



If the true result is larger than the mean of results the bias is negative, and if the true result is smaller than the mean of results the bias is positive.

Generally, bias is influenced by systematic variations within the analytical determination. For example, those introduced when a consistently smaller volume or mass is dispensed than would otherwise be expected to be dispensed. This might occur for instance if a balance was used that was not calibrated correctly and instead of using an amount of substance weighing exactly 5.00 g, only 4.86 g was actually weighed and dispensed. If this process were repeated many times, it may be found that 4.79, 4.91, 4.73, 4.86, 4.82, 4.70, 4.89 and 4.77 g were actually dispensed.

Knowledge of the actual true concentration of a particular parameter in a sample is rarely available. The bias of an analytical determination can be estimated by analysing a certified reference material, CRM, and comparing the result obtained in the laboratory with the stated result. A matrix certified reference material is a sample which has undergone repeated analyses often by many different and independent analysts using a variety of methods. Following this lengthy and costly process a certificate is issued, with associated confidence, that the material contains a stated amount of the parameter determined, i.e. deemed the true value. To complicate matters, the actual or true result may be expressed as a range of values distributed in a Gaussian manner. In the laboratory using the method in question, the CRM is analysed and the result obtained is compared with the stated CRM value, and then the bias determined, either as an absolute value, or as a percentage value. See Appendix 2. The matrix of the CRM chosen should be very similar to the matrix of the samples to be analysed and contain similar concentrations of the parameter being determined in the sample. The task of locating such a suitable matrix CRM is often difficult, time-consuming and expensive and a compromise is often made finding a CRM that is close to but not exactly as required.

### 5.3. RECOVERY

Recovery is an alternative way of expressing bias, and can be estimated by analysing a sample and then repeating the analysis following a known addition of the parameter to the sample. The concentration,  $C_S$ , determined in the sample prior to the spiked addition, is then compared with both the concentration,  $C_{WS}$ , of the sample following spiked addition, and the resulting calculated increase in the concentration,  $C_{ISA}$ , after the spiked addition. From these values the recovery is calculated. See **Appendix 2**.

Recovery values of less than 100% indicate negative bias whilst recovery values greater than 100% indicate positive bias.

However, care should be exercised in determining recovery data. For example when a substance (representative of the parameter to be determined) is added to a sample for spiking purposes, it may behave differently to the naturally occurring parameter already present in the sample. For example, the naturally occurring parameter may be strongly adsorbed to particulate matter in the sample. Any added substance may only become weakly adsorbed. Thus, following addition of the substance, and prior to any possible subsequent treatment procedure, the spiked sample should be left to equilibrate. When the spiked sample has equilibrated the extraction and determination should be completed in such a manner that all or most of the parameter is extracted and determined. In addition, the recovery of an added substance may be affected by the nature of the matrix to which it is added. Only by undertaking the analyses and generating data, will confirmatory evidence be made available to demonstrate whether this is the case. Recovery tests should therefore be undertaken on matrices similar to the samples being analysed, and at concentration levels appropriate to the concentrations routinely determined.

### 5.4. UNCERTAINTY OF MEASUREMENT

As mentioned previously, when a sample is analysed many times a range of different values is usually obtained. There is, therefore, a degree of uncertainty in the result that could be reported, from the many replicated results recorded. It is an essential part of good laboratory practice that this uncertainty should be evaluated as part of method validation and any result should be quoted with an indication of its uncertainty of measurement. An estimate of this uncertainty is essential if the result is to be compared with a critical level of interest to ascertain if the result is above or below this critical level. This critical level may be a prescribed regulatory limit, such as an EQS value, or an operator-imposed level, such that process control can be monitored. Alternatively, this critical level may be a permit concentration value agreed with the competent authority. The uncertainty of measurement can be expressed and estimated using several techniques, see Appendix 2. Some of these techniques are statistically based, for example a 95% confidence interval obtained from a student's two-sided t-test, others less so scientifically based. Uncertainty of measurement is one of the performance characteristics [5] used as performance criteria for assessing the quality of methods used for monitoring purposes and establishing laboratory and analyst capabilities.

Where the uncertainty of measurement is reported for a particular concentration, this will affect other calculations based on this concentration. For example, the load of a particular parameter released into the environment over a period of time is often based on the concentration of the parameter in the effluent and the flow rate of the effluent discharged into the environment. Thus, where a concentration is used to determine the load, then the load calculated using this concentration, will also exhibit an UoM. A measure of the load UoM will reflect a combination of the concentration UoM and flow rate UoM, and will probably be similar in magnitude to the greater of these UoM values, which is probably the concentration UoM. Generally, concentration UoM values far exceed flow rate UoM values.

### 5.5. LIMIT OF DETECTION

The limit of detection (LoD) concentration is the smallest concentration of parameter that can, with reasonable confidence, be determined in a sample. Concentrations below this concentration cannot be reported with any degree of certainty or confidence. By definition therefore, it is impossible to state that when a determination has been carried out, the concentration is zero and that therefore the parameter is not present in a sample. The best scenario that can be reported is to state that a parameter may be present at a concentration above zero but below the LoD concentration. Any concentration that is determined and is found to be above the LoD concentration can be reported with a stated degree of confidence as a positive result. An exception to this occurs in situations when a reporting system, involving a minimum reporting value or limit of quantification (LoQ) is used, see section 5.6, and the concentration is above the LoD but below the MRV or LoQ value. A concentration that is determined and found to be below the LoD concentration that is determined and found to be below the LoD concentration that is determined and found to be below the LoD concentration that is determined and found to be below the LoD concentration should be reported as "less than LoD concentration". If a minimum reporting system is used, and the concentration is found to be between the LoD and

LoQ concentrations, it should be reported as "less than LoQ concentration". The QA/QC Directive describes the LoD somewhat differently as "the output signal or concentration value above which it can be affirmed, with a stated level of confidence that a sample is different from a blank sample containing no determinant of interest". This presupposes that a blank sample can be prepared and that it will not contain the determinant of interest.

An estimate of the LoD concentration can be made by analysing blank samples that are taken through all of the analytical procedures. The standard deviation, s<sub>b</sub>, obtained from these blank determinations is calculated, and then multiplied by a factor to give the LoD concentration. The factor used is usually between 3 and 5 and depends on the statistical confidence applied to the determination. For example, both the international standard ISO TS 13530 [17] and the guide for chemical laboratories on in-house method validation [18] use a factor of 3. An Environment Agency MCERTS performance standard [19] reports a factor of 5.1. Where the limit of detection is a critical issue, it should be evaluated using a more rigorous approach [20]. See Appendix 2. An alternative approach to calculating LoD values is to define the LoD in terms of the signal to noise ratio [21] of the instrument used in the analytical determination. A measure of noise is the difference between the highest and lowest values of the measured signal when no parameter is present. Usually, the signal to noise ratio is multiplied by a factor, usually, between 3 and 5, to give the LoD value. This approach however, depends on the technique used in the determination and is not appropriate for all methods.

Thus the determination of LoD values and their reporting can be a very confusing issue. This is further complicated when LoD values are then used to define LoQ values. See below and section 5.6.

The LoD determination for a particular method usually depends on such factors as instrument sensitivity and matrix effects of the sample being analysed. Consequently, different LoDs are usually obtained by different methods and can be different even if the same technique or method is used but involves different instruments or equipment.

Depending on the techniques used in the analysis, it may be more appropriate to use samples or solutions containing a small amount of parameter, instead of blank samples. This should be of a low but known concentration. The use of blank samples, or samples or solutions containing a small amount of the parameter close to the blank value, may lead to different values of the LoD being determined. Differences in these values may or may not be significant. Over time, repeated analyses for LoD values will lead to differences in their concentrations being determined. To overcome the reporting of these different LoD values, a system is devised whereby the LoD is multiplied by a factor, usually between 2 and 4, to encompass any maximum differences likely to be encountered. The resulting value is then known as the limit of quantification, and is the single minimum reporting value that is used for reporting purposes. See section 5.6.

Usually an analysis is undertaken to ascertain whether a result generated is above or below a critical level of interest. This critical level may be a prescribed regulatory limit, such as an EQS value, or an operator-imposed level, such that process control can be monitored. Alternatively, this critical level may be a permit concentration value agreed with the competent authority. When assessing the suitability of a particular method, especially to ensure with confidence that a result is below this critical level, then throughout the analytical community it is generally recognised that a method with a LoD concentration of less than 10% of the critical level of interest would be fit for purpose. Thus, in the case of benzene where an AA-EQS is prescribed with a value of 10  $\mu$ g/l, a method with a LoD of 1  $\mu$ g/l would be deemed acceptable. A method with a LoD of 3  $\mu$ g/l might be considered less acceptable, but may still be adequate.

Where interested parties, such as a competent authority or operators representing a specific industrial sector, need to compare the performance data of their methods used to analyse environmental or effluent samples, all parties should agree a common definition for the limit of detection. These parties should also agree how this concentration value should be calculated.

#### 5.6. LIMIT OF QUANTIFICATION

As previously mentioned in sections 5.1 and 5.2, when day to day determinations of the LoD are carried out there are, usually, slight differences in the values determined. Over a period of time these different LoD values will cover a small range which might be distributed in a Gaussian or normal manner. To overcome the reporting of different LoDs for a particular parameter, and to avoid the confusing observation of many different "less than LoD concentration" values being reported, a reporting system is often devised whereby only a single minimum concentration is reported. This system involves defining a limit of quantification, LoQ, (or sometimes referred to as a minimum reporting value, MRV). The LoD value is multiplied by a factor such that all anticipated LoD values determined over time are expected to be no more than the LoQ calculated. The factor chosen is usually between 2 and 4, but is somewhat arbitrary. This factor equates to approximately 10-times s<sub>b</sub>, the standard deviation of the blank measurement. For example the international standard ISO TS 13530 [17] reports that the LoQ is 3 times the LoD value, whereas the guide for chemical laboratories on in-house method validation [18] reports the LoQ to be 5, 6 or 10 times the standard deviation of the blank measurement. Another publication [21] reports the LoQ to be 2.5 times the LoD, and a Nordtest report [16] uses LoQ as twice the LoD, as does a Royal Society of Chemistry [22] publication. An Environment Agency MCERTS performance standard [19] reports LoQ to be 5 times the LoD. See also Appendix 2.

The LoQ reporting system is simply an aid to avoid confusion arising from different LOD concentrations being determined for the same method. Whilst its use can be beneficial, it is not essential. One issue of using a minimum reporting value is that a protocol needs to be agreed for any result that is determined and recorded, and found to be between the LoD and the LoQ or minimum reporting value. This specific value may be lost at the reporting stage, when it is simply reported as "less than LoQ concentration". This loss may either be for future use, i.e. where a mean value needs to be calculated, or alternatively, for immediate use, i.e. where an absolute discharge, i.e. the load of a parameter is required, and which may be based on concentrations and flow rates of particular discharges to the environment. In addition, "less than LoQ" values cannot be averaged or added, in cases where periodic, for example annual, average values need to be calculated, unless a reporting system is specifically defined to cover this issue, for example as prescribed in legislation [5]. Another issue that needs to be addressed when considering the use of such a minimum reporting system is how to deal with results that are found to be

- i) Below the LoD concentration;
- ii) Between the LoD concentration and the LoQ concentration.

For situations in i) above the result can either be reported as less than the LoD concentration, or as less than the LoQ concentration if a minimum reporting system is used. For situations in ii) above the result can either be reported as less than the LoQ concentration if a minimum reporting system is used, or as the result actually determined if a minimum reporting system is not used.

Alternatively, other protocols can be agreed, for example, for situations in i) above the result can be reported as zero, or other fraction of the LoD concentration. For situations in ii) above the result can be reported as half the LoQ concentration or other fraction of the LoQ concentration, if a minimum reporting system is used.

Whichever protocol is adopted is somewhat arbitrary, however its use needs to be consistently applied across a specific organisation or sector.

One of the consequences of using LoQs, that themselves can be calculated in several ways (based on LoDs, which also can be calculated in several ways), is that any other calculation based on these LoQ values will itself also exhibit a variety of values, each depending on which LoQ value is used. For example, a concentration may be determined and used to calculate a load, i.e. the amount of parameter released over a period of time into the environment. If a concentration is recorded and found to be above the LoD concentration but below the LoQ value, then the concentration may therefore be "lost" but the reported concentration may then be used to calculate a load. The load value calculated will depend on how the LoQ is defined, which itself also depends on how the LoD is calculated. A very confusing situation thus develops which causes severe problems when comparisons of data are being studied and evaluated. See also section 6.

Where interested parties, such as a competent authority or operators representing a specific industrial sector, need to compare the performance data of their methods used to analyse environmental or effluent samples, all parties should agree a common definition for the limit of quantification. These parties should also agree how this concentration value should be calculated and how it is to be applied for selective reporting purposes.

### 5.7. OTHER PERFORMANCE CHARACTERISTICS

In addition to the performance characteristics already mentioned, there are other characteristics that are important for assessing a method's use and include features such as sensitivity, drift, scope, specificity, selectivity, linearity, range of application, ruggedness, etc. Whilst these characteristics influence the way a method operates the impact of each of these features is not as significant as that resulting from precision, bias etc.

#### 5.8. METHOD VALIDATION

Before any comparison of parameters, methods or results can be undertaken, basic statistical concepts and how they are applied to laboratory practices need to be understood. In addition, before any method can be used routinely within a laboratory, that method should be performance tested within the laboratory to ensure staff can generate results that demonstrate they can assure themselves that the method can perform satisfactorily in their own laboratory, and on their own particular type of matrices. Methods should be assessed in this way before any real samples are analysed and results reliably reported. This process should be carried out whether the method is a national, international or European standard, other

published method (which has been validated independently by others) or an inhouse developed method. This process, commonly referred to as method validation, comprises a number of procedures encompassing a variety of techniques.

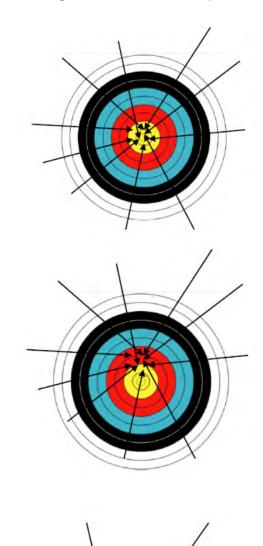
Generally, when a sample is analysed on a routine basis, it is done so only once. Occasionally, duplicate analyses may be carried out. From these analyses it is impossible to obtain information on performance characteristics, such as precision and bias that is of any meaningful value to which confidence can be attributable to. Hence the need to validate the method first to determine these performance characteristics before the determination is carried out on real samples. Only by properly validating a method before it is used routinely can a measure of its suitability be assured, and results that are fit for purpose, be generated.

Once a method has been characterised in terms of its performance and this is deemed to be satisfactory, it can be used for analysing samples. In order to ensure that the method remains in control and continues to generate results that are in line with its established capability, on-going quality control (QC) samples or solutions should be analysed at the same time that samples are analysed. Analysis of these QC samples provides evidence that the method is being used properly, or highlights potential changes that might occur, that would otherwise remain un-noticed.

**Figure 4** highlights the importance of validating methods before they are used routinely to analyse samples. As previously referred to, samples are rarely analysed more than once, thus, plots of the sort shown in **Figure 4** cannot be produced and information on the method capability gathered.

Thus, in order to possess prior knowledge of precision and bias before samples are analysed, validation of the method is essential. When replicated analyses are carried out on a sample, **Figure 4** shows the results that may be obtained and how they may be plotted. The true result is deemed to be at the centre of the dart board, and the results are represented as a scatter-plot.

Figure 4



Plots of precision and bias

This diagram shows the scatter of results to be close together, and that the mean is close to the centre.

The plot indicates good precision, and as the mean of the results is close to the centre, indicates a negligible bias.

Ideally, a method should reflect this pattern, in order to generate reliable and reproducible results.

This diagram shows a similar scatter of results that are close together, but that the mean is displaced from the centre.

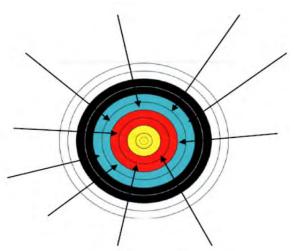
Whilst this plot indicates good precision, the mean of the results is offset from the centre, indicating a significant bias.

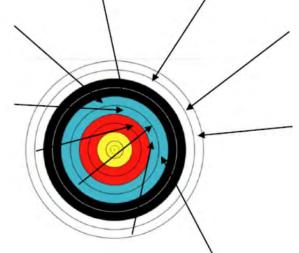
If the bias is shown to be constant over time, the mean result could be corrected before being reported.

This diagram shows the scatter of results to be widely dispersed, with the mean, perhaps fortuitously, close to the centre.

The plot indicates poor precision, and as the mean of the results is close to the centre, indicates negligible bias. However, this may be coincidental.

A method reflecting this pattern should not be used or should be amended and changed in order to try and improve its performance.





This diagram shows a similar scatter of results that are widely dispersed, with the mean displaced from the centre.

The plot indicates poor precision, and as the mean of the results is offset from the centre, shows a significant bias.

A method reflecting this pattern would be classed as a poor method and should not be used or should be amended and changed in order to try and improve its performance.

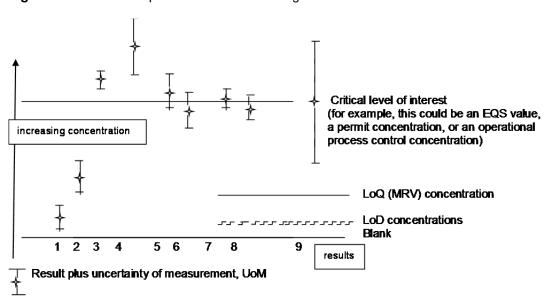
Validation involves a process whereby repeated analyses, often in small batches, are carried out over a period of time. The number of replicated analyses is referred to as the number of degrees of freedom, DoF. This number represents a measure of the degree of confidence that can be attributable to the results. The larger the number of DoF the more confidence can be attributable. However, there is a balance. Too few replicate analyses result in limited confidence that can be assured. Too many analyses and the return in confidence that can be attributable may not be cost effective in terms of the additional resources required to gain very little additional information.

It is recognised within the analytical community that at least 10 degrees of freedom is sufficient to produce results to an acceptable level. It is known that analysing 11 batches of samples in duplicate (involving 22 repeat analyses) will always produce a minimum of number of 10 DoF. Other combinations, for example analysing 4 batches of samples in triplicate, may not always produce this minimum number of degrees of freedom. The actual number of degrees of freedom will depend on factors such as the within-batch variation of analyses and the betweenbatch variation.

Where interested parties, such as a competent authority or operators representing a specific industrial sector, need to compare the performance data of their methods used to analyse environmental or effluent samples, all parties should agree and adopt a common core of procedures for validating their methods, and calculating such performance characteristics as precision, bias and recovery etc.

### 5.9. DECISION MAKING PROCESS

As mentioned previously, an analysis is usually undertaken to ascertain whether a result generated is above or below a critical level of interest. This critical level may be an EQS value, a concentration agreed under a permit condition, or a concentration used for process control or operational purposes. In order to have confidence that a result is below this critical level then both the concentration reported using a particular method and its uncertainty of measurement should be known, and both the result and its associated UoM should be completely below the critical level concentration. See the results 1 and 2 in **Figure 5**.



*Figure 5* Interpretation of a result being above or below a critical level

In the case of result 1, the result could be reported as "less than LoQ concentration" as this value lies between the LoD value and the LoQ value.

In order to have confidence that a result is above a critical level then both the concentration reported and its uncertainty of measurement should be known, and both the result and its associated UoM should be completely above the critical level concentration. See the results 3 and 4 in **Figure 5**.

In both these cases for results 1 and 2, and for results 3 and 4, a definitive decision can be made with confidence. Even though the concentration represented by result 4 may have been generated using a method whose performance is considered to be less than the performance of the method used to generate result 3, a definitive decision can still be made as to it being above the critical level. This demonstrates that the method used to generate result 4, even though considered inferior to the method used to generate result 3, is still fit-for-purpose at this concentration level.

Only where the result and its uncertainty of measurement overlaps the critical level will doubt exist as to whether the result actually reported should be considered to be above or below the critical level. See the results 5 and 6 in **Figure 5**. Whilst an improvement in the method's performance will lead to a reduction in the uncertainty of measurement, the uncertainty surrounding the decision making process at concentrations close to the critical level of interest will never be removed, only reduced. See the results 7 and 8 in **Figure 5**.

An example of where the uncertainty of measurement is found to be large relative to the critical level of interest is shown by result 9, which illustrates an UoM of about 50% of the critical level. In this case, confidence in the result would be quite low as a result found to be close to the critical level would show its associated lower limit of the UoM to be very close to the LoQ value, which is regarded as the minimum reporting value for a LoD value considered acceptable in relation to the critical level.

The results in **Figure 5** show that even with a method that is considered inferior to others, a definitive decision can still be made using it, provided the performance of the method, including its associated uncertainty of measurement, is well established, and documented before it is used routinely for analysing samples.

## 6. OPINION ON THE STATISTICAL INTERPRETATION OF RESULTS

Over a period of time a series of results may be obtained in which a decision needs to be taken on whether

- i) A regulatory breach has occurred, for example the EQS value;
- ii) A permit concentration has been contravened; or
- iii) An operational process control level has been exceeded.

For each parameter analysed, the critical level of interest may be a corresponding EQS value, a maximum or periodic average permit concentration agreed under a permit condition, or an operator self-imposed maximum or periodic average concentration level used for process control or operational purposes.

If it is assumed that a series of results has been determined, say on a bi-monthly basis, and  $x_1$ ,  $x_2$ ,  $x_3$ ,  $x_4$ ,  $x_5$  and  $x_6$  represents the results obtained over a one-year period, and associated with each of these results is an estimation of the uncertainty of measurement, u, then the reported results might be  $x_1 \pm u_1$ ,  $x_2 \pm u_2$ ,  $x_3 \pm u_3$ ,  $x_4 \pm u_4$ ,  $x_5 \pm u_5$  and  $x_6 \pm u_6$ . Each of these results may be treated independently as illustrated in **Figure 5**.

If the UoM is greater than 50% of the concentration value representing the relevant EQS value then, from a WFD and QA/QC Directive perspective, this would be a breach of the requirements. This only needs to be applied when samples are taken in accordance with the requirements of the WFD. In addition, if the LoQ calculated for these results is greater than 30% of the corresponding EQS value, then this would also be a breach of the requirements. Again this only applies for samples taken in accordance with the requirements of the WFD. Where no EQS value is prescribed for a particular parameter these requirements would not apply. If the same criteria outlined in the QA/QC Directive were to be applied to, for example process control levels, then this may also be a breach of these self-imposed criteria, but would not be legally binding.

If each result of the example above is greater than the defined LoQ concentration, then the mean value,  $x_A$ , is given as

 $x_{A} = (x_{1} + x_{2} + x_{3} + x_{4} + x_{5} + x_{6}) / 6$ 

This mean value may, for example, represent a periodic or annual average value.

If one of the results, for example  $x_3$ , is found to be below the LoQ concentration, then  $x_3 = LoQ$ , and the mean value,  $x_{A_1}$  calculated according to the requirements of the QA/QC directive would be given as

 $x_{A} = (x_{1} + x_{2} + x_{4} + x_{5} + x_{6} + (LoQ / 2)) / 6$ 

If, in this example, all 6 results are below the LoQ value, then

 $x_{A} = (3 \times LoQ) / 6$ 

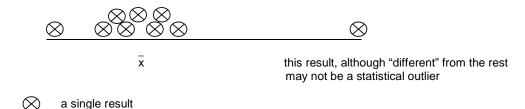
If, as above, the mean value is calculated and found to be below the LoQ, then, according to the requirements of the QA/QC directive, the mean value shall be reported as "less than LoQ".

If the annual average value of the determinations is above the corresponding AA-EQS value then from a WFD or QA/QC Directive perspective a regulatory breach of the legislation [6], would occur. If a single result, for example  $x_5$  is found to be above the corresponding MAC-EQS value then this would also be a breach of the legislation [6]. The same, or similar, criteria might also be applied to permit concentrations or operational process control levels, and if so, would cause a contravention to occur. However, if different criteria were used, for example, as indicated in section 5.6, different findings would result.

Notwithstanding the quality of the method used and the analytical performance established, provided the result has been generated within statistical control as demonstrated by appropriate analysis of quality control samples, and provided the uncertainty of measurement of the result is known and documented, it is possible to establish whether a result is above or below a critical level of interest. See **Figure 5**.

When, during these analyses a result is generated that appears different or inconsistent with the rest of the results, then there may be a suspicion that this result could be regarded as being an outlier, see **Figure 6**. There are several statistical tests that can be carried out to confirm or disprove this view. However, results should never be discarded purely on a statistical basis, and evidence should always be sought to find the cause of the disparity. Only if this evidence suggests that an error has been made in the analysis and the statistical test confirms the result to be an outlier, should the result be discarded. If there is no supporting evidence the result should be included with all the others.

*Figure 6* Establishing presence of outliers



If all of the results are generated under statistical control, (demonstrated by the analysis of sufficient quality control samples that are shown to be satisfactory) then it is extremely unlikely that the result, deemed to be different from the rest, should be discarded, whether confirmed as a statistical outlier or not, unless supported by investigatory evidence obtained following the determination. The presence of such a result should always instigate an investigation, and the result should only be rejected if a discernible cause can be identified and the statistical test confirms it as an outlier. The fact that a result appears different or anomalous is not sufficient reason for rejecting that result as its presence does not necessarily mean that it is an outlier. This will depend on several factors such the amount of data available, i.e. the number of results, their quality and the range of values observed.

Once a result is suspected of being different, a valid reason should always be sought to account for its unusual or abnormal presence. In addition, if results of quality control samples show that the analysis is not in control, then irrespective of whether the result can be considered an outlier or not, the result should be investigated and reasons found to account for the out of control condition. There are several statistical techniques that could be used to demonstrate whether a result is an outlier or not. Such outlier tests include Dixon's test, Grubbs' test, Nalimov's test, Walsh's test, Cochran's test and Bartlett's test, and the use of any test should be judged on individual merits and circumstances. The outcomes of each test, i.e. whether results are deemed statistical outliers or not, depend on whether a calculated critical value for the test is higher or lower than a tabulated value devised for that test. Details of such tests can readily be found in most statistical text books [23,24] or on the internet by inserting the name of the test into suitable search engines.

Whilst many analyses are carried out, for many purposes the ultimate requirement of this data may not be the concentration values themselves, but other features reliant on knowledge of these concentrations. For example, the total load of a parameter released into the environment following discharge of an effluent over a period of time is based on knowledge of the concentration of the parameter in the effluent and the flow rate of the effluent being discharged. The load can thus be based on a single concentration value, for example  $x_4$  in the above example and the flow rate at the time of sampling, or on an average concentration value,  $x_A$ , and the average flow rate of the flow rates at the time of each sampling event.

Using the above example, and assuming the flow rate of the effluent being discharged into the environment at the same time as the concentration is determined is F, then the load, L, is given by

 $L = x_4 \times F$ 

Appropriate factors can be used so that if units of concentration are expressed in  $\mu g/l$  and units of flow are expressed in m<sup>3</sup>/hour, then the amount released into the environment can be expressed, for example in units of kg/year.

A consequence of expressing concentrations with associated UoM values is that there will be corresponding uncertainty in the associated load values calculated. The greater the concentration UoM, the greater will be the UoM of the load calculated. Therefore, if there is little confidence in the concentration determined, there will be little confidence in the load calculated using this concentration. In addition, if a method is used where the LoD is reported to be 5  $\mu$ g/l, and the LoQ is defined as 3-times this value, i.e. 15  $\mu$ g/l, and following analysis, a concentration is found to be say 7  $\mu$ g/l, and then using these values, for example, a load needs to be calculated, then the load will depend on which protocol (as indicated in section 5.6) is used. As well as taking into account the UoM of the analysis, there is also uncertainty resulting from the protocol used. The load calculated will vary depending on whether 7.5  $\mu$ g/l is used or whether 15  $\mu$ g/l is used. The resulting loads calculated will vary by a factor of at least 2 using the protocols outlined in section 5.6. If corresponding flow rates of the effluent are very large, the estimated load calculated may not adequately represent the true value released into the environment.

### 7. METHOD CAPABILITIES

### 7.1. PARAMETER ANALYSIS

Within the legislative frameworks outlined in section 2, there are requirements that discharges to the environment should be monitored, and the concentrations or annual loads of selected parameters should be determined, recorded, and often reported to external organisations, such as competent authorities. A survey conducted by CONCAWE in 2011 shows that its members analysed a wide selection of parameters, see **Table 1**, totalling 61 parameters. Most of these parameters are prescribed in at least one of the legislative frameworks indicated in section 2. Several other parameters which are not specifically mentioned or referenced in these frameworks were also analysed by some of the oil refinery operators. Whether the choice of these parameters that were analysed by different site operators reflects individual circumstances at different sites across Europe, or different regulatory regimes applied by different competent authorities, or a combination of these factors, is less clear.

### 7.2. PARAMETERS AND METHODS MENTIONED IN THE CONCAWE SURVEY

**Appendix 1** lists those analytical methods cited in the CONCAWE survey [3] used for the parameters reported in the survey. Also shown (in italic red font) in this appendix are details of other methods that have not been cited in the survey but which could have been used, as methods showing similar performance capabilities to the methods cited, where performance data have been obtained for these methods. These other methods were identified following a brief literature review of environmental methods used for aqueous discharges to the environment. Only those parameters cited in the CONCAWE survey were reviewed in the literature. At least one method for each parameter has been added and included in the list of methods cited in the survey. Where performance data could be obtained, the quality of the methods listed in **Appendix 1** has been compared and assessed, and prioritised in order of their analytical capabilities. See section 7.4 and **Appendix 3**.

Where a national, or dual national and international standard, or dual national and European standard has been cited in the CONCAWE survey, reference is given to the international or European standard, or dual European and international standard. Often a standard is published as a triple joint national European international standard. National standards are invariably based on the corresponding international or European standard, but not necessarily with the same numbering system. Sometimes a different numbering system is used for the international standard and the national standard, at other times the same numbering system is used. For example, ISO 11083 - Water quality - Determination of chromium (VI). Spectrometric method using 1,5-diphenylcarbazide, is also referenced as BS 6068-2.47. Also, the ISO standard, ISO 17993:2002 - Water quality - Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction, is the same as the dual European and international standard EN ISO 17993:2003, which is identical to the joint German European and international standard DIN EN ISO 17993-2004, the only differences being the year of publication.

However, to complicate matters more, the use of the same numbering system sometimes refers to a different standard. For example, the British Standard BS 6468 - Specification for depth micro-meters, possesses the same number as the British European and international standard BS EN ISO 6468 - Water quality - Determination of certain organo-chlorine insecticides, polychlorinated biphenyls and chloro-benzenes - Gas chromatographic method after liquid-liquid extraction. However, this joint triple standard is also referenced as British Standard BS 6068-2.57. Similar confusion also arises with other European numbering systems. Where a national standard is mentioned in the CONCAWE survey, the corresponding international or European standard with the same title is referred to in **Appendix 1**, with or without the same numbering system.

### 7.3. METHOD ASSESSMENT PROGRAMME

To address the concerns on the suitability and performance of the cited methods in the survey an assessment of the methods listed in **Appendix 1** has been carried out. This assessment prioritises the methods in order of their analytical capabilities and provides an overall ranking of the methods. This ranking exercise is based on selected characteristic features, namely precision, bias or recovery, LoD (where appropriate), indicative cost and ease of use. These features were chosen as representing those different qualities of the methods that could be used as a basis for judging their suitability.

These characteristic features are banded into a defined band or range of values representing decreasing quality within the feature under consideration. For example, costs have been banded as low, medium and high cost, depending on the complexity of the technique used and equipment required. Each band or range of values within the feature is then given a ranking score as a means of quantifying each band. Using the same example, a low cost analysis is given a ranking score of 1, and a medium cost analysis is given a ranking score of 2, etc. In the programme each feature has been assigned four bands, and each band can be clearly distinguished from each other. The ranking scores of each feature are then added together producing an overall ranking value for that method. The method with the lowest overall ranking value of all methods is deemed to be the best method for determining that parameter.

Where no information on a specific characteristic feature is available for a particular method, this band has been given the highest ranking score so that this places the ranking of this band below those of the other bands or ranges where information is available, even if the information forthcoming is considered of poor quality. The principle being adopted is that any information that is available, irrespective of its quality, is better than no information.

In addition, where an appropriate EQS value has been prescribed [6] for a particular parameter an indication is provided on whether each method satisfies the requirements for the LoQ and UoM prescribed in the QA/QC directive [5]. This indication is given purely for informational purposes and is based on specific definitions for the LoQ and UoM (as shown in section 7.3.3.6). In these cases, the LoD is included in the ranking exercise, but where no EQS value is prescribed, the LoD is not included in the ranking exercise. Similarly for process control levels used for operational purposes, or permit concentration values agreed with the competent authority. In these cases, the same LoQ and UoM criteria have been used although there may not be the regulatory requirement. Where no concentration for the critical level of interest is given, no assessment of the LoQ or UoM requirement is given.

Where exceptional health and safety issues are deemed a cause for concern during the operation of a method, these issues are also highlighted in the programme. It should be recognised, however, that not all these issues can be addressed in this programme, as often too little detail is contained within the detail of the method.

Because the primary basis of the assessment programme is centred on the analytical performance capability, characteristic features such as precision, and bias or recovery are deemed much more important than LoD, indicative cost and ease of use. The characteristic features precision, and bias or recovery, have therefore been given a larger weighting in terms of their ranking scores. For example, the highest quality band or range for these features is set a ranking score of 10. For the other features, namely LoD (where appropriate if an AA-EQS value is prescribed) indicative costs and ease of use, the equivalent band or range is set a ranking score of 1. In this way, differences in the precision and bias or recovery of different methods (and hence their placement in the different quality bands or ranges) causes a more pronounced effect on the overall ranking value than differences in the other features.

If users were to consider that the characteristic features identified above should be prioritised differently in terms of their importance, then this view can be accommodated. For example, if the LoD were to be considered as important as precision and bias or recovery, then the ranking scores of this feature can be changed to reflect this. In addition, if different bands or ranges were to be considered, these could also be changed. Having made these changes to the assessment programme, the programme would need to be re-run and a new ranking determined. The assessment programme allows users to change both the banding or range values of the characteristic features chosen to represent different qualities of the method, and also the ranking scores for these bands or ranges. Changing these bands or ranges, and associated ranking scores, enables different comparisons to be made based on users' own priorities. For example, if laboratories wished to concentrate more on features like indicative costs or the ease of use of a particular method rather than on its analytical performance capability, different ranking scores can be assigned to these features.

An alternative approach that can be adopted instead of undertaking method comparisons to the one just described is to establish whether the results obtained using one or more methods are equivalent [24]. Adopting this approach, however, is much more analytically challenging for laboratories, and involves numerous analyses of identical samples using a variety of methods.

### 7.3.1. Matrix effects

Whilst this assessment process highlights the more favourable methods in terms of their performances, whether the cited capability can be matched by the individual laboratory would need to be demonstrated by the laboratory. In addition, whether the cited capability reflects that which could be obtained following analysis of oil refinery effluents would also need to be demonstrated by the laboratory concerned. The performance data of the methods mentioned in the CONCAWE survey have been generated usually on matrices such as drinking water, river, ground water and municipal waste effluents, spiked standards etc. If known, an indication of the matrix on which the performance data is generated is included in the programme. It should be clearly understood however, that data generated for these matrices may not be able to be matched by performance data generated on oil refinery effluents. The future benefit of use of the assessment programme lies in laboratories being able to input details of their own methods and their own performance data for their own

matrices rather than rely on data that may not be appropriate for their specific analyses. Since information on oil refinery effluent matrices is not available, generally, no indication can be provided on whether the methods assessed are strictly applicable to oil refinery effluents and whether they can be used routinely for this purpose.

Where interested parties, such as a competent authority or operators representing a specific industrial sector, need to compare the performance data of their methods used to analyse environmental or effluent samples, all parties should agree to provide details of the methods they use and the performance data obtained on their own specific effluents, so that appropriate and realistic method assessment comparisons can be undertaken.

It is further suggested that these parties establish a "control group" to collate appropriate information relevant to the specific sector to provide this information so that the assessment programme can be regularly updated with new data, enabling methods to be compared that are more directly applicable to a specific sector.

The matrices indicated in the methods cited in the CONCAWE survey are given in **Table 3**.

DW	drinking water
GW	ground water
RW	river water
ReW	reagent water
AS	aqueous solution
AdW	acid-digested water
WW	waste water
IE	industrial effluent
SE	sewage effluent
SS	synthetic standard
Ū	Unknown

**Table 3**Matrices quoted in methods cited in the CONCAWE survey for<br/>which performance data are available

As can be expected these matrices are vastly different to oil refinery effluents and performance data generated on these matrices may be significantly different to data generated for oil refinery effluents, even though the same methods might be used.

### 7.3.2. Parameter definitions

It is an essential feature of the assessment programme, that if it is to be used effectively, then methods that are to be compared for a particular parameter must be based on a like-for-like basis. The parameter determined must therefore be identical and be clearly and unambiguously defined. Without establishing this criterion, it is meaningless trying to assess and compare methods that do not relate to the same parameter being determined. See also sections 3 and 9.4.

### 7.3.3. Method characteristic features and their ranking scores

The overall ranking value derived in the assessment programme for each method is based on ranking scores for the following characteristic features:

- i) precision;
- ii) bias or recovery;
- iii) limit of detection, where appropriate (i.e. whether a critical level is given);
- iv) indicative cost of analysis; and
- v) ease of use.

Some analyses can be considered much more difficult than others. For example, the determination of organic compounds is often more demanding than the determination of metals and similar parameters such as inorganic compounds. Recognising this, for organic analyses, different bands or ranges have been used in the ranking exercise for the characteristic features precision, bias and recovery than those used for non-organic analyses. This is to reflect the more challenging task of undertaking organic analysis, compared to non-organic analysis. Whilst bands or ranges for organic analyses are made less demanding than corresponding bands or ranges for non-organic analyses, the same ranking scores have been used. For example, for organic analyses, the highest quality range for recovery is set at 90-110%, for non-organic analyses the equivalent range is set at 95-105%. However, both ranges have been given the same ranking score of 10. This does not invalidate this approach for organic and inorganic analyses but recognises the differences in the complexity of the analyses between these types of analyses. If other users were of the opinion that there was little difference between organic and non-organic analyses, in terms of their complexities or challenges, identical bands or ranges could be made for both organic and non-organic parameters.

Another characteristic feature of a method is its applicability. Whether a particular method is applicable to either a number of different matrices, or alternatively, to numerous different concentration levels can only be demonstrated by generating performance data on samples where the nature of the matrix and the concentration levels differ significantly. It is often the case that where an original method is used and performance data generated for a particular matrix, then modifications, however slight, might need to be made to the method in order for it to be used to obtain equivalent performance data on a different matrix. Of course, when modifications are made to a method, it then becomes a different method. Since the nature of oil refinery effluents will probably differ from site to site and different concentration levels are found at different sites, the applicability of the method cited in the survey has not been assessed in the method assessment programme to establish whether the cited method is suitable for the analysis of oil refinery effluents.

Identified below are the ranking profiles for the methods reported in the 2010 CONCAWE survey.

### 7.3.3.1. Precision

Precision values for each method are placed within three specific bands or ranges, representing different qualities of prescision. Each range is then assigned a ranking score based on these banding values. See **Table 4**.

Quality of band or range	Corresponding precision band or range for organic analyses	Corresponding precision band or range for non- organic analyses (metal and similar determinations)	Ranking score
	%	%	
Highest	0 to 10	0 to 5	10
Medium	>10 to 25	>5 to 20	20
Lowest	>25	>20	30
No information available			40

#### **Table 4**Precision ranges and ranking scores

As indicated, the bands for organic analyses are less stringent than those for nonorganic analyses to reflect the more demanding determination, and where no information is available a higher ranking score is given. For a particular method where it is noted that the precision is quoted in the same units as the result, this value would need to be converted to a percentage value. Where it is indicated that the method precision varies with the concentration, and different performance data have been generated for different concentrations, an average value of the precision values has been used to reflect the different concentrations. Thus, for a particular organic parameter, if a method exhibits a precision of say 3.9%, then the precision value is assigned a ranking score of 10. If, for a different method, the precision is quoted as 16.7%, the precision is assigned a ranking score of 20. If no information is available for the precision, a ranking score of 40 is assigned.

Where interested parties, such as a competent authority or operators representing a specific industrial sector, need to compare the performance data of their methods used to analyse environmental or effluent samples, and obtain the greatest benefit using the assessment programme, all parties should agree on the values of these ranges and ranking scores for precision, or agree and adopt an alternative set of values.

#### 7.3.3.2. Bias or recovery

Bias values for each method are placed within three specific bands or ranges representing different qualities of bias. Each range is then assigned a ranking score based on these banding values. Recovery values for each method are placed within five specific bands or ranges representing different qualities of recovery. Each range is then assigned a ranking score based on these banding values. However, since bias and recovery can be recognised as being the same, only one of these criteria, i.e. bias or recovery, is used in the method assessment programme. If information on both is available recovery values are used. See **Tables 5 and 6**.

### Table 5Bias ranges and ranking scores

Quality of band or range	Corresponding bias band or range for organic analyses	Corresponding bias band or range for non- organic analyses (metal and similar determinations)	Ranking score
	%	%	
Highest	0 to 10	0 to 5	10
Medium	>10 to 25	>5 to 20	20
Lowest	>25	>20	30
No information available			40

#### Table 6 Recovery ranges and ranking scores

Quality of band or range	Corresponding recovery band or range for organic analyses	Corresponding recovery band or range for non- organic analyses (metal and similar determinations)	Ranking score
	%	%	
Highest	90 - 110	95 - 105	10
Medium	75 to <90 and >110 to 125	80 to <95 and >105 to 120	20
Lowest	<75 and >125	<80 and >120	30
No information available			40

As indicated, the bands for organic analyses are less stringent than those for nonorganic analyses to reflect the more demanding determination, and where no information is available a higher ranking score is given. For a particular method where it is noted that the bias is quoted in the same units as the result, this value would need to be converted to a percentage value. Where it is indicated that the method bias or recovery varies with the concentration, and different performance data have been generated for different concentrations, an average value of the bias or recovery values has been used to reflect the different concentrations. Thus, for a particular organic parameter, if a method exhibits a recovery of say 98.6%, then the recovery value is assigned a ranking score of 10. If, for a different method, the recovery is only 78.1%, the recovery is assigned a ranking score of 20. If no information is available for the recovery, a ranking score of 40 is assigned.

Where interested parties, such as a competent authority or operators representing a specific industrial sector, need to compare the performance data of their methods used to analyse environmental or effluent samples, and obtain the greatest benefit using the assessment programme, all parties should agree on the values of these ranges and ranking scores for bias and recovery, or agree and adopt an alternative set of values.

### 7.3.3.3. Limit of detection

Generally, LoQ values are not usually quoted with performance data when a method is published, hence LoD values have been used in the assessment programme, as these values are more readily available. Limit of detection values for each method are placed within three specific bands or ranges, representing ranges based on percentage values of the annual average EQS value. Each range is then assigned a ranking score based on these relative percentage values. See Table 7. Where no information is available a higher ranking score is given. For this exercise, the AA-EQS value has been chosen to represent the Critical Level of Interest (CLoI), as these values are known. However, the critical level could equally be represented by a maximum or periodic or annual average permit concentration agreed under a permit condition, or a maximum or periodic average process control level used for process control or operational purposes. As described in section 7.4, the bands, ranking scores and the relative percentage values can all be changed by users to reflect their own priorities. As pointed out in section 5.5, a LoD of 10% of the critical level of interest would be deemed acceptable, other percentage values less so acceptable.

Table 7	Recovery ranges and ranking scores
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Quality of band or range	LoD as % of CLoI	Ranking score
Highest	0 to 10	1
Medium	>10 to 30	2
Lowest	>30	3
No information available		4

For this characteristic feature the ranking scores for these bands are smaller than the coresponding bands for precision, bias and recovery. This is to reflect the importance given to analytical capability rather than to the more subjective LoD feature of the method.

Where there is no EQS value, ranking of the LoD is not included in the method assessment programme. Effectively, this means that if there is no critical level of interest, ranking of the LoD values is not included in the method assessment.

Thus, for a particular parameter, if a method exhibits a LoD of say 0.9  $\mu$ g/l and the critical level of interest, for example an AA-EQS value is 10  $\mu$ g/l, then the LoD value is assigned a ranking score of 1. If, for a different method, the LoD is 5  $\mu$ g/l, the LoD is assigned a ranking score of 3. If no information is available for the LoD, a ranking score of 4 is assigned.

Where interested parties, such as a competent authority or operators representing a specific industrial sector, need to compare the performance data of their methods used to analyse environmental or effluent samples, and obtain the greatest benefit using the assessment programme, all parties should agree on the values of these ranges and ranking scores for limit of detection, or agree and adopt an alternative set of values.

### 7.3.3.4. Indicative costs

An indicative cost for each method is placed within one of three specific bands. This cost is usually based on sample preparation, treatment and method technique used for the determination. Usually the more complex the anaysis, the more the cost of this analysis. The higher the cost, the higher the ranking score assigned to it. See

**Table 8**. This cost, whilst based on real figures is somewhat subjective and is given as low, medium or high cost, represented as  $\in$ ,  $\in \in$  and  $\in \in \in$  respectively. Where no information is available a higher ranking score is given.

Cost of analysis	Indicative cost	Ranking score
Low	€	1
Medium	€€	2
High	€€€	3
No information available		4

For this characteristic feature the ranking scores for these bands are smaller than the coresponding bands for precision, bias and recovery. This is to reflect the importance given to analytical capability rather than to this more subjective feature of the method.

For a particular parameter, if the cost of the analysis is considered to be low, then the indicative cost value is assigned a ranking score of 1. If, for a different method, the cost is high the indicative cost is assigned a ranking score of 3. If no information is available for the cost of the analysis, a ranking score of 4 is assigned.

Where interested parties, such as a competent authority or operators representing a specific industrial sector, need to compare the performance data of their methods used to analyse environmental or effluent samples, all parties should agree boundaries for these bands by establishing real costs for distinguishing between low, medium and high costs of analysis. They should also agree on the ranking scores for indicative costs.

### 7.3.3.5. Ease of use

An indication is also given on how easy the method is to operate. Features of its use include the time taken to prepare reagents and samples, how quickly results can be reported, the complexity of operations needed to generate solutions for determination etc. The easier the method is to operate, the lower the ranking score assigned to it. See **Table 9**. This indication is purely subjective and is given as easy, less difficult and difficult and is represented as  $\bigcirc \bigcirc \odot \odot$ ,  $\bigcirc \odot$  and  $\odot$  respectively. Where no information is available a higher ranking score is given.

Table 9	Ease of use and ranking scores
---------	--------------------------------

Quality of band	Ease of use	Ranking score
Easy to use	$\odot$ $\odot$ $\odot$	1
Less difficult to use	00	2
Difficult to use	$\odot$	3
No information available		4

For this characteristic feature the ranking scores for these bands are smaller than the coresponding bands for precision, bias and recovery. This is to reflect the importance given to analytical capability rather than to this more subjective feature of the method. For a particular parameter, if the method is considered easy to use, then the ease of use value is assigned a ranking score of 1. If, for a different method, the method is considered difficult the ease of use value is assigned a ranking score of 3. If no information is available to judge how, a ranking score of 4 is assigned.

Where interested parties, such as a competent authority or operators representing a specific industrial sector, need to compare the performance data of their methods used to analyse environmental or effluent samples, all parties should agree on the ranking scores for ease of use.

### 7.3.3.6. LoQ and UoM compliance

Only when samples are required to be submitted according to the requirements of the WFD need an assessment be made for LoQ and UoM compliance. If samples are not to be submitted according to the WFD requirements, then compliance with the QA/QC Directive need not be assessed. In assessing LoQ compliance with the requirements of the 2009/90/EC directive [5] the following definition has been made in the method assessment programme.

 $LoQ = 3 \times LoD$ 

where LoD is the limit of detection reported for the parameter and individual method. A factor of 3 has been used as this value reflects a typically average factor quoted in many publications, see section 5.5. This calculated LoQ is the figure used and compared to the corresponding LoQ figure given in **Table 1** based on the AA-EQS value for that parameter. The use of this definition recognises that in the directive [5] no definition is prescribed and no further guidance offered to regulators. In addition, often in the methods cited in the CONCAWE survey there is no information available to show how the LoD has been calculated. This impacts on the LoQ calculation and it may be that differences in LoQ values, as well as reflecting differences in how LoQs are calculated, also reflects differences in how the LoD is calculated in different methods. This is another reason why LoD values have been given lower priority, in terms of their ranking scores, compared with precision and bias or recovery. See also sections 5.5 and 5.6.

In assessing compliance with the UoM requirement [5], this criterion has been defined as

 $UoM = 3 \times s \tag{1}$ 

where s is the precision of the method. This calculated UoM is the figure used and compared to the corresponding UoM figure given in **Table 1** based on the AA-EQS value for that parameter. This definition is chosen over other similar definitions that could be used as over 99% of results that could be expected are covered by  $\pm 3$  standard deviations, see section 5.1, and if this criterion satisfies the legislative requirements it is expected that the other calculations that could be used would also satisfy the requirement.

These approaches reflect the failure in the directive [5] to adequately define these criteria.

Where an EQS value for a particular parameter is not prescribed, no assessment for compliance with the LoQ and UoM requirements in the directive is carried out in the method assessment programme.

Whilst the above definition for the UoM is used, it is recognised that confusion will arise over the issue of whether the UoM compliance requirement will be satisfactory or not, if other definitions are used, for example

 $UoM = (2 \times s) + |bias|$ (2)

It is found that where a method shows that the precision is poor but recovery is good, then depending on actual values of the precision and recovery, the UoM compliance requirement can be satisfactory using equation 2, but not satisfactory using equation 1. For example the US EPA method 602 for benzene quotes precision to be 20% and recovery to be 93%. Using these values in equations 1 and 2, shows different conclusions for the UoM compliance requirement.

Whilst LoQ and UoM compliance are assessed they are not included in the ranking exercise and have not been assigned ranking scores.

In addition, if no information is available for the bias or recovery of a particular method but the precision is shown to be good, then the use of equation 1 may show the UoM compliance requirement to be satisfactory, but if equation 2 were to be used, results would show that no assessment of the compliance requirement can be made.

Where interested parties, such as a competent authority or operators representing a specific industrial sector, need to compare the performance data of their methods used to analyse environmental or effluent samples, and obtain the greatest benefit using the assessment programme, all parties should agree on a common definition of uncertainty of measurement and how it should be calculated.

### 7.3.4. Method assessment

Listed in **Appendix 3** are summaries the results of the method assessments carried out for the parameters provided in the CONCAWE survey where performance data could be obtained. Appendix 4 contains details of the actual assessments. **Tables 10, 11, 12, 13 and 14** highlight typical examples of this method assessment programme. The examples chosen reflect organic analyses for parameters for which an AA-EQS value is prescribed (for example benzene) and for which an AA-EQS value has not been prescribed (for example TPHs). In addition, examples also reflect non-organic analyses for parameters for which an AA-EQS value is prescribed (for example the data have been inputted for a particular parameter, the assessment programme prioritises the methods in ranking order of their analytical capabilities, based on the ranking scores given in section 7.3 assigned for each characteristic feature of the method.

Where an AA-EQS value is prescribed for a particular parameter and there is no information or data on the performance of a specific method, then an overall ranking value of 92 will be established. This would be based on ranking scores for precision, bias or recovery, LoD, costs and ease of use of 40, 40, 4, 4 and 4 respectively. This would represent a method of the lowest quality and be of the lowest priority. Where a method is reported to show very good precision and recovery, exhibits an acceptable LoD in terms of its associated critical level, and is cheap to operate and very easy to use, then ranking scores 10, 10, 1, 1 and 1 would be assigned and an overall ranking value of 23 will be established. This would represent a method of the highest priority. Depending on the quality of the method, an overall ranking value of between 23 and 92 will be expected. Thus, the

actual overall ranking value itself is not an important factor, but the relative positions of the methods are important.

Where an AA-EQS value is not prescribed for a particular parameter and there is no information or data on the performance of a specific method, then an overall ranking value of 88 will be established. This would be based on ranking scores for precision, bias or recovery, costs and ease of use of 40, 40, 4 and 4 respectively. This would represent a method of the lowest quality and be of the lowest priority. Where a method is reported to show very good precision and recovery, and is cheap to operate and very easy to use, then ranking scores 10, 10, 1 and 1 would be assigned and an overall ranking value of 22 will be established. This would represent a method of the highest quality and be of the highest priority. Depending on the quality of the method, an overall ranking value of between 22 and 88 will be expected. Thus, the actual overall ranking value itself is not an important factor, but the relative positions of the methods based on their ranking values are important.

Where the analytical performance of any of the methods assessed satisfies both of the LoQ and UoM compliance requirements [5] as defined in section 7.3.3.6, then these methods would be suitable for compliance monitoring under the WFD. This is provided the data generated on the matrices analysed matches or is better than the data generated using the matrices quoted in the assessment programme. See also section 7.3.1.

**Appendix 4** in this report contains the actual method assessments which are summarised in **Appendix 3**.

### 7.3.4.1. Organic analysis for benzene, a priority substance for which an AA-EQS value is given

Details for nine methods have been assessed, see **Table 10**. Since there is an AA-EQS value [6] the UoM compliance requirement [5] needs to be assessed, and LoD estimations need to be taken into account to assess the LoQ compliance requirement [5].

Of the nine methods assessed and compared, eight are mentioned in the CONCAWE survey and one other (namely, MEWAM 170) has been added as a method that could have been used for monitoring benzene. One method, EN ISO 10301, not listed in the table but mentioned in the survey did not show any performance data for this parameter.

Five methods, EN ISO 15680, US EPA 502.2, US EPA 524.2, US EPA 8260 and MEWAM 170 satisfy both the regulatory UoM and LoQ compliance requirements [5] as defined in section 7.3.3.6.

Of these five methods, four methods, EN ISO 15680, US EPA 502.2, US EPA 524.2 and US EPA 8260 are shown to be clearly better than the rest in terms of their overall ranking values (each with ranking values of 25) based on their precision and recovery values. One method, MEWAM 170 was rated slightly less (overall ranking value of 35) due to a poorer precision value.

One method, US EPA 624, did not satisfy either of the UoM or LoQ compliance requirements [5] as defined, and was rated next poorest of all methods (overall ranking value of 37) due to a poor precision value and a high LoD value. Two other methods, US EPA 602 and US EPA 8020 satisfy only one of the compliance requirement [5], namely the LoQ requirement, as defined, and were rated slightly

less (each with overall ranking value of 35) than the better methods due to poorer precision and recovery values. ISO 11423-1 was rated the poorest method (overall ranking value of 46) due to poor precision and recovery.

As mentioned in section 7.3, if users wish to change the ranges or ranking scores to reflect their own priorities, the assessment programme allows users to do this. **Table 14** shows a method assessment undertaken with LoD ranking scores being treated equally with precision and bias and recovery. In this case, **Table 14** shows the ranking scores to be the same for LoD, i.e. 10, 20, 30 and 40 respectively as for the same corresponding ranges used for precision and bias and recovery. As expected, the overall ranking values have changed for each method, but not, on this occasion, the relative positions of the methods.

### 7.3.4.2. Organic analysis for TPH, that has no AA-EQS value

This is a classic example of methods being compared which should not be treated in this way. Whilst the assessment of the methods for this parameter (and similar parameters) is easy to undertake, see **Table 11**, the exercise is in-approriate as a like-for-like comparison is not being made. Any interpretations resulting from it should be treated with the utmost caution. See also section 9.4.4.

The problem with this type of analysis is that the term OiW or TPHs comprises many hundreds of different compounds and is not a single substance. As mentioned in section 9.4.4 one of the many difficulties associated with TPH analysis is that there is no single determination that can be used to measure all of the TPH compounds that may be present in a sample. In addition, the term TPHs covers a range of hydrocarbon compounds and unless clearly and unambiguously defined is a meaningless term to use. Since the methods used in the assessment tool prioritisation process are very different in respect of the substances and compounds being determined it is clearly quite meaningless to undertake a direct comparison of all the method performances. The method used will dictate the result obtained, thus changing the method will produce a different result. The results may be a correct value for what is being determined, but what is being determined is different for each different method. See also section 3.

Method EN ISO 9377-2 is based on a solvent extract of the sample, which is then cleaned-up using Florisil to remove non-hydrocarbon substances and polar compounds. The clean extract is then determined using CG with FID and gives a measure of the hydrocarbon content, both aliphatic and aromatic (including toluene, ethylbenzene, the xylenes and PAHs) and naphthenic compounds, all eluting between  $C_{10}H_{22}$  and  $C_{40}H_{82}$ , i.e. *n*-decane and *n*-tetracontane respectively.

Methods MEWAM 77 and SM 5520C however, are based on a non-hydrocarbon solvent extract of the sample which is then determined by IR spectroscopy at selected wavelengths. Method MEWAM 77 reports the use of Florisil (to clean-up the extract and remove non-hydrocarbon and polar compounds) but SM 5520C does not. Thus the SM 5520C extract may contain non-hydrocarbon substances that have been extracted and reported as hydrocarbons, even though they are not. The hydrocarbons included in both these determinations may include those less than  $C_{10}$  and greater than  $C_{40}$  which are not accounted for in method EN ISO 9377-2. Method SM 5520F is similar to these methods but the solvent extract is cleaned-up using silica gel, and then determined gravimetrically following evaporation of the solvent. Other methods mentioned in the survey are based on similar techniques to the ones just described. A notable exception is method UNE EN 1484. This method is based on the measurement of TOC which is then determination is calibrated for

TPHs is not clear. Also, included in this TOC measurement might be other organic compounds that are not TPHs, and it is unclear whether this is taken into account or not.

Thus not only are different methods used, but the methods determine different substances and groups of substances, all of which are referred to by a single term, OiW or TPHs. The fact that different methods have been used is not the issue; it is simply in-appropriate to compare TPH methods where different definitions have been used to define the parameter TPH.

### 7.3.4.3. Non-organic analysis for nickel, a priority substance for which an AA-EQS value is given

Details for ten methods have been assessed, see **Table 12**. Since there is an AA-EQS value [6] the UoM compliance requirement [5] needs to be assessed, and LoD estimations need to be taken into account to assess the LoQ compliance requirement [5].

Of the ten methods assessed and compared, eight are mentioned in the CONCAWE survey and two others (namely, MEWAM 46 and MEWAM 163) have been added as methods that could have been used for monitoring nickel.

Only three methods, US EPA 200.8, MEWAM 163 and US EPA 6020, satisfy both the regulatory UoM and LoQ compliance requirements [5] as defined in section 7.3.3.6. However, these three methods are clearly shown to be ranked quite differently with overall ranking values of 25, 35 and 65 respectively. Methods US EPA 200.8 and MEWAM 163 differ slightly in their recovery values, whilst for method US EPA 6020 there is no recovery information available.

Whilst several other methods, for example EN ISO 15586, ISO 17294, US EPA 200.7 and ISO 11885 (overall ranking values of 26, 28, 37 and 38 respectively) show ranking values similar to the two better methods, their LoD values do not satisfy the legislative requirement for LoQ, as they are either too high or information is not available.

The ranking of other methods, for example, US EPA 6010, MEWAM 46 and ISO 8288 (overall ranking values of 47, 57 and 58 respectively) either reflect their precision values or a general lack of information being available on recovery or LoD values. The ranking of method US EPA 6010 reflects poor precision and high LoD value; the ranking of method MEWAM 46 reflects good precision but high LoD value and no information on recovery, whilst the ranking of method ISO 8288 reflects good precision but no information for LoD and recovery values.

### 7.3.4.4. Non-organic analysis for vanadium that has no AA-EQS value

Details for six methods have been assessed, see **Table 13**. Since there is no AA-EQS value both the LoQ and UoM compliance requirements [5] need not be assessed.

Of the six methods assessed and compared, all of which are mentioned in the CONCAWE survey, three methods, EN ISO 15586, ISO 17294 and US EPA 6010 are shown to be clearly better than the rest in terms of their overall ranking values (each with a ranking value of 24) based on their precision and recovery values. Two methods, US EPA 200.7 and US EPA 200.8 were rated slightly less (overall ranking value of 34 and 44 respectively) mainly due to poorer recovery values.

The method ranked last, US EPA 6020 (overall ranking value of 74) shows very poor precision and no information available for recovery.

### 7.3.4.5. Other parameters

Similar tables for each of the parameters mentioned in the CONCAWE survey and shown in **Table 1**, and for all of the methods indicated in **Appendix 1** where performance data has been available are presented in **Appendix 4**.

These tables are based on the performance capabilities of the methods for the matrices indicated and not on the performances established by oil refinery operators' own laboratories, which may be significantly different. Only by properly validating the procedures in their own laboratories will laboratories demonstrate that they can match or improve upon the performances cited. When this information is generated and established by individual oil refinery operators, these values can then be inputted into the assessment programme enabling an operator to ascertain the position of its own method within the prioritised list of methods, recognising that cited performances may not be applicable to oil refinery effluents. As already pointed out the performances generated by the cited methods are based on the analyses of drinking waters, ground waters, river waters etc and not on oil refinery effluents and as such may be significantly different to the performances generated by these methods on refinery effluents.

For some parameters, for example, BTEX, PAHs and similar parameters where groups of compounds are measured, these parameters are not included in the assessment programme, but appear only as individual compounds. This is to ensure a like-for-like comparison is undertaken, unlike the one described in section 7.3.4.2. Thus, benzene, toluene, ethyl benzene and ortho, meta and para xylenes appear individually in the assessment programme, but BTEX does not. The analysis of parameters like BTEX is generally undertaken in a single operation, and whilst it is recognised that these parameters may be reported as single group parameter or group of compounds, methods for these determinations can only be assessed adequately on an individual parameter basis. See also section 7.3.2.

Typical assessment of methods for the organic parameter, benzene, for which an AA-EQS value is given (This assessment should be compared with the one in Table 14) Table 10

input, as appropriate into the yellow-shaded area, the type of analysis as Organic or Non-organic

Organic

Input, as appropriate into the yellow-shaded area, the name of parameter

# BENZENE

input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of yg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

A4-Eq5 Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

RANKING OVERALL ORDER \*\*\*\*\* Ease of Use 000 000 000 000 000 000 000 000 Indicative cost <del>..........</del> If 0, does not comply **UoM Requirement** UoM = 3 x s 50 % of CLoI If 0, does not comply LoQ, Requirement LoQ = 3 x LoD 30 % of CLoI ---0 -Limit of detection 0.2 10.0 4.4 0.2 0.14 2 Recovery 92.6 92.6 104 6 6 97 97 R ŝ æ Precision 3.9 1.6 5.7 2.0 2.0 2.0 2.0 1.1.7 R Matrix GW ReW ReW - X - X A Method reference EN ISO 15680 US EPA 302.2 US EPA 324.2 MEWAM 170 US EPA 8260 US EPA 8020 **US EPA 624 US EPA 602** 

If 2, no UoM requirement

If 2, no LoQ requirement

If 1, complies

If 1, complies

DW drinking water GW ground water RW river water ReW reagent water A aqueous solution AdW waste water WW waste water IE industrial effluent SE synthetic standard U unknown Typical assessment of methods for the group organic parameter, TPH for which an AA-EQS value is not given Table 11

Input, as appropriate into the yellow-shaded area, the type of analysis as Organic or Non-organic

Organic Input, as appropriate into the yellow-shaded area, the name of parameter

OiW or TPH

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/I. This could be an EOS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank

Input data for each r	nethod as ap	propriate into the ye	ellow-shaded	area, if no data	Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank					
Method reference Matrix Precision	Matrix	Precision	Bias	Recovery	Recovery Limit of detection	LoQ=3×LoD	UoM = 3 × 5	Indicative cost Ease of Use	Ease of Use	OVERALL
		*	*	*	He/	LoQ, Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of CLoI			ORDER
EN ISO 9377-2	5	6.5		82		2	2	æ	000	34
MEWAM 77 A	ន	3.1		99.4	8	2	2	ЭЭ ЭЭЭ	000	24
SM 5520 D	×	7.9		88		2	2	ЭЭЭ	000	34
SM 5520 F	ß			97.2		2	2	ж	000	2
SM 5520 C	×	10		66		2	2	ж	000	24
						If 0, does not comply	If 0, does not comply			
						If 1, complies	If 1, complies			
						If 2, no LoQ requirement If 2, no UoM requirement	If 2, no UoM requirement			

DW drinking water GW ground water RW river water REW reagent water AS aqueous solution AdW acid-digested water AdW acid-digested water Be industrial effluent SE synthetic standard U unknown Typical assessment of methods for the non-organic parameter, nickel, for which an AA-EQS value is given Table 12

Input, as appropriate into the yellow-shaded area, the type of analysis as Organic or Non-organic

input, as appropriate into the yellow-shaded area, the name of parameter

Non-organic

NICKEL

4

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units or Jg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

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Input, as appropriate	e into the yell	low-shaded area, wh	hether this is an	EQS value, pen	mit concentration, pro	input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.	me, leave blank.			
AA-EQS										
Input data for each n	method as ap	input data for each method as appropriate into the yellow-shaded area, if no data available leave blank	ellow-shaded an	ea, if no data a	vailable leave blank					
Method reference	Matrix	Precision	Bias	Recovery	Recovery Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
		×	8	*	hg/i	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of CLoI			ORDER
US EPA 6020A		6.4			0.03	1	-	eee	000	8
US EPA 6010C	AdW	10.3		94.3	10	•		999	000	47
ISO 11885	WW	1.6		92.1		•	-	555	000	R
US EPA 200.8	51	4.1		97.8	0.06	1	-	eee	000	22
US EPA 200.7	5	2		92.5	•	•	-	555	000	37
MEWAM 46	DW	2.8			43	•	-	666	000	57
MEWAM 163	×	4.8		16	0.13	1	-	999	000	8
ISO 8288	ReW	m				•	-	666	000	8
EN ISO 13386	WW	4.2		66	1	•	-	eee	000	26
ISO 17294	S	4.3		86		•		999	000	28
						If 0, does not comply If 1, complies	If 0, does not comply If 1, complies			
						If 2, no LoQ requirement	If 2, no UoM requirement			
THE WALLS WITH										

DW drinking water GW ground water RW river water ReW reagent water AS aqueous solution AdW acid-digested water WW acid-digested water WW acid-digested water E industrial effluent SE sewage effluent SS synthetic standard U unknown

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Input, as appropriate into the yellow-shaded area, the type of analysis as Organic or Non-organic

Input, as appropriate into the yellow-shaded area, the name of parameter

Non-organic VANADIUM Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/I. This could be an EOS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropr	iate into the	yellow-shaded area	a, whether this	is an EOS value,	permit concentration, pr	Input, as appropriate into the yellow-shaded area, whether this is an EOS value, permit concentration, process control level or other. If none, leave blank	f none, leave blank.			
Input data for eat	ch method as	appropriate into th	he yellow-shade	ed area, if no dat	Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank					
Method	Matrix	Precision	Bias	Recovery	Recovery Limit of detection	LoQ=3×LoD	UoM=3xs	Indicative cost Ease of Use	Ease of Use	OVERALL
reference		8	*	29	<b>H</b>	LoQ. Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of CLoI			ORDER
EN ISO 15586	WW	11		102	2	2	2	ŧ	000	24
ISO 17294	ង	4.7		6.79		2	2	eee	000	24
US EPA 200.7	ш	1.25		87		2	2	ŧŧ	000	34
US EPA 200.8	ш	0.05		75.5	6.0	2	2	eee	000	44
US EPA 6020A	Å	45.5			0.03	2	2	ŧŧ	000	74
US EPA 6010C	AdW	1.9		<u> 99.3</u>	2	2	2	ŧŧŧ	000	24
						If 0, does not comply	If 0, does not comply			

If 2, no UoM requirement

If 2, no LoQ requirement

If 1, complies

If 1, complies

AdW acid-digested water ReW reagent water AS aqueous solution IE industrial effluent DW drinking water GW ground water WW waste water RW river water

SE sewage effluent SS synthetic standard

U unknown

Typical assessment of methods for the organic parameter, benzene, for which an AA-EQS value is given, and where LoD has been given the same ranking scores as precision, bias and recovery Table 14

(this assessment should be compared with the one in Table 10)

Input, as appropriate into the yellow-shaded area, the type of analysis as Organic or Non-organic

## Organic

Input, as appropriate into the yellow-shaded area, the name of parameter

## BENZENE

Input, as appropriate into the yellow-shaded area, the critical level of interest (Ctol) in units of µg/I. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank,

## AA-EOS

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

%         %         %         %         Mg/l         Lod Requirement         UoM Requirement         CANKING           EN ISO 15680         GW         104         0.1         1         1         1         0         000 EN         33           US EP \$20.2         ReW         97         0.01         1         1         1         1         000 EN         33           US EP \$20.2         ReW         97         0.01         1         1         1         1         33         000 EN         33           US EP \$20.2         ReW         97         0.04         1         1         1         1         1         33           US EP \$20.2         U         97         0.04         1	Method reference Matrix	Matrix	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost Ease of Use	Ease of Use	OVERALL
GW         104         0.1         1 <th></th> <th></th> <th>24</th> <th>*</th> <th>µ2H</th> <th>LoQ, Requirement 30 % of CLoI</th> <th>UoM Requirement 50 % of CLoI</th> <th></th> <th></th> <th>RANKING</th>			24	*	µ2H	LoQ, Requirement 30 % of CLoI	UoM Requirement 50 % of CLoI			RANKING
ReW         97         0.01         1         1         1         1         000           ReW         97         0.04         1         1         1         1         1         000           NeW         97         0.04         1         1         1         1         1         1         000           U         92.6         0.2         1         0         0         1         1         1         1         1         1         1         1         0 <td< td=""><td>EN ISO 15680</td><td>GW</td><td></td><td>104</td><td>0.1</td><td>1</td><td>1</td><td><b>H</b></td><td>000</td><td>33</td></td<>	EN ISO 15680	GW		104	0.1	1	1	<b>H</b>	000	33
Rew         97         0.04         1         1         1         1         00           U         92.6         0.2         1         0         <	US EPA 502.2	ReW		25	0.01	T	1	<b>H</b>	000	33
U         92.6         0.2         1         0         €         000           AS         97         0.04         1         1         1         1         0         €         000           V         95         4.4         0         0         0         €         000         €         000         000         €         0000         000         €         0000         0000         €         0000         0000         €         0000         0000         €         0000         0000         €         0000         0000         €         0000         0000         €         0000         0000         €         0000         0000         €         0000         €         0000         0000         €         0000         €         0000         0000         €         0000         €         0000         0000         €         0000         0000         €         00000         0000         €         00000         0000         0000         €         00000         0000         0000         0000         0000         0000         0000         0000         0000         0000         0000         0000         00000         0000         0000	US EPA 524.2	ReW		26	0.04	1		<b>H</b>	000	R
AS         97         0.04         1 <td>US EPA 602</td> <td>0</td> <td></td> <td>92.6</td> <td>0.2</td> <td>- (F)</td> <td>0</td> <td><b>3</b></td> <td>000</td> <td>43</td>	US EPA 602	0		92.6	0.2	- (F)	0	<b>3</b>	000	43
U         95         44         0         0         €         000           AS         92.6         0.2         1         0         €         000         €         000         000         €         0000         000         €         0000         €         0000         €         0000         €         0000         €         0000         €         0000         €         0000         €         0000         0000         €         0000         0000         €         0000         €         0000         0000         €         0000         0000         €         0000         0000         0000         €         0000         0000         €         0000         0000         0000         0000         €         00000         0000         €         00000         00000         0000         0000	US EPA 8260	SA		16	0.04	1	1	<b>H</b>	000	33
AS 92.6 0.2 1 1 0 €€ 0.00 DW 104 0.14 1 1 1 €€ 0.00 If 0, does not comply If 0, does not comply If 1, comples If 1, comples	US EPA 624	n		55	4.4	0	0	<b>H</b>	000	8
DW IO4 0.14 1 I E E UDU If 0, does not comply If 0, does not comply If 1. complies If 1. complies	US EPA 8020	SA		92.6	0.2	I	0	<b>#</b>	000	43
	MEWAM 170	DW		101	0.14	1	I	#	303	43
						If 0, does not comply If 1. complies	If 0, does not comply If 1. complies			

If 2, no UoM requirement

If 2, no LoQ requirement

DW drinking water GW ground water RW river water Rew reagent water AS aqueous solution AdW acid-digested water WW waste water IE industrial effluent SE sewage effluent SS synthetic standard

U unknown

### 8. PARAMETER COMPARISON

From the information obtained in the CONCAWE survey, a study of the data reveals that there is no consistent approach adopted between the site operators and their individual choices of parameters monitored. This is not unexpected, as, whilst oil refinery operations would generate effluents that might possess common features, it should be recognised that no two effluents would necessarily be identical, i.e. consist entirely of the same matrix, and hence, require exactly the same analysis. The results of the survey would seem to support this view.

Oil refinery operators across Europe might be expected to analyse a common core of parameters to reflect the common features of the effluents and the requirements of directives which equally apply to all members states. However, other analyses that should also be carried out might be different at different sites, to reflect the differences in the matrix composition of the effluents. This inconsistent approach may also be a reflection of the different permits granted by individual competent authories for the different members states.

The justifiable variability in the analyses carried out by oil refinery operators across Europe probably results from the different permits granted by different competent authorities, and may be a reflection of the difficulties in the interpretation of illdefined and poorly expressed parameters, as cited in the legislative frameworks identified in section 2. Furthermore, the observed approaches might reflect the individual choice of parameters selected by the operators that reflect the differences in the nature of the effluents generated, that in turn reflect the fact that there are no two refineries that possess the same configuration, operating strategy, product portfolio and type of crude-oil intakes, that all affect the efficient operation of an oil refinery.

### 9. ANALYTICAL INTERPRETATIONS

Of the 61 parameters included in the CONCAWE survey, 51 of the parameters should not be a cause for concern. The different methods used for their analysis should not be a problem to oil refinery operators, as these parameters are clearly and unambiguously defined. Because the different methods used should determine the same parameter, any variability noted in the analytical performances of each method can be attributable to either the different procedures used and/or to laboratory and analyst capabilities. If the methods used for a single parameter are comparable in their analytical performances, irrespective of the procedures used, and assuming laboratory and analyst capabilities are also similar, then comparable results should be generated. If laboratory and analyst capabilities are similar but comparable results are not observed, this may be a reflection of the different procedures used, i.e. the methods, and their individual analytical performance capabilities.

Of the 51 parameters it is noted that for 21 of them there is no specific reference to them in the legislative frameworks identified in section 2, see **Table 1**, i.e. they are non-specific in that they are not clearly identified in the legislation. It is probably the case that these parameters are covered by general requirements to monitor non-specifically identified parameters.

For the remaining 10 parameters (see **Table 15**) however, there may be a cause for concern in the interpretation of the analytical results produced, as these results are dependent on the method applied, or the definiton used for the parameter under consideration.

Parameter	Cause of concern
AOX	instrumental technique
BOD	standard method
COD	standard method
extractable substances with petroleum ether	method defined result
free cyanide	method defined result
OiW or TPHs	method defined result
PAHs	method defined result
phenols	method defined result
TOC	instrumental technique
toxic metals	method defined result

Table 15         Parameters where interpretational concerns n	hay be important
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### 9.1. BOD AND COD

Of the 10 parameters referred to in section 9, two, namely BOD and COD, can be categorised using standard methods, either as national, international or European standards. Across Europe individual countries are responsible for producing their own national standards. For example, in the UK, the British Standards Institution (BSI) is responsible for publishing a British Standard (BS). In Germany, the equivalent responsibility resides with the Deutsches Institut für Normung (DIN). National standards are based on international (ISO) standards or European (CEN) standards and should be written in such a way as to ensure that all analyses are

carried out in exactly the same way. Thus any differences in analytical performances can be attributable to laboratory or analyst capabilities and not the fact that different procedures have been used. These standards are usually published as national, international, European, or dual national and international standards, or dual national and European standards. For example, in the case of the parameter BOD, ISO 5815:1989 (BS 6068-2.14:1990 - Water Quality - Physical, chemical and biochemical methods - Determination of biochemical oxygen demand after 5 days) is now replaced by EN ISO 1899-1:2008 (BS 6068-2.63:1998 - Water Quality - Determination of biochemical oxygen demand (BODn). Dilution and seeding method with allylthiourea addition.) Since these parameters are determined essentially using the same procedures, then comparable results should be generated provided laboratory and analyst capabilities are similar.

Similar factors apply to the determination of COD, although this situation is more complicated by the use of test kits that have been developed by various manufacturers, that mimic the use of standard COD methods and purport to generate equivalent results. Only when performance data generated using test kits are shown to be equivalent to the performance data generated using standard methods should their use be condoned.

### 9.2. TOC AND AOX

Procedures used for the routine determination of the parameters TOC and AOX, are usually based on instrumental techniques developed by different manufacturers. These techniques generate results that are often used as surrogate results for the estimation of contamination. These results do not provide direct information on the exact nature of the pollutant or its true concentration, but are useful for determining trends in concentration levels.

In the case of TOC, these techniques may employ different oxidative temperatures, different catalysts, different detection systems, etc. The use of these different techniques may result in different results being generated even for the same sample. Unless data are available to show that comparable results can be generated using different manufacturer's instruments, it should not be assumed that inherent comparability will arise for all methods where TOC is determined.

Similar factors apply to the determination of AOX, which is a technique generally performed in non-UK countries across Europe, rather than in the UK.

### 9.3. METHOD DEFINED PARAMETERS

For the remaining parameters shown in table 8, for example toxic metals, TPH and extractable substances with petroleum ether, the methods used will define the results obtained. Changing some of the procedures or conditions within the method may lead to a change in the results obtained. With these types of parameters several fundamental issues need to be addressed before a comparison of results can be undertaken.

### 9.3.1. Toxic metals

In the case of toxic metals, the choice of metals that are to be determined would need to be known, i.e. which specific metals are to be compared across the operators? For any comparions to be meaningful, the choice of metals selected would need to be identical in all cases, and a harmonised approach adopted across all sites. Assessors would need to be confident that "like-for-like" comparisons are to be made. As an analogy, there is little point comparing a box of apples and pears with a basket of oranges and lemons.

Furthermore, for a specific metal determination, this generally involves either a "total" determination or a procedure to determine only the soluble fraction of the total content present. Metals can be present in the aqueous phase of the sample, or be adsorbed onto the surface of particulate matter in suspension within the aqueous phase. It would need to be ascertained which fraction is being determined and reported.

With certain matrices and under certain conditions, extraction techniques, i.e. addition of concentrated acid or mixture of acids, can generate results that are very similar to the results generated using "total" determinations. However, with other samples and conditions, vastly different results can be generated between extraction techniques and "total" determinations. This situation depends entirely on the matrix effects of the individual samples and the methods used. Data would need to be available before routine analysis could begin, to demonstrate that suitable comparisons can be made.

For the soluble fraction, the sample would need to be filtered before analysis begins, and for comparison exercises, the nominal pore size of the filter would need to be the same for all analyses. This is to ensure that the particulate size of the suspended matter removed from the sample is the same. Soluble fractions often rely on the addition of concentrated acid or mixture of acids. Determinations for "total" fractions generally require a digestion stage using a choice of chemical treatments under various conditions.

From a legislative point of view, there is no requirement for the parameter, toxic metals, to be monitored. It is noted only one oil refinery operator presented data for the parameter toxic metals, but provided no indication of which metals had been determined.

### 9.3.2. Phenols

Whilst this specific group of compounds is prescribed in the legislation identified in section 2, no additional information is given to indicate which individual phenols are to be monitored. From the data provided in the CONCAWE survey no meaningful comparisons can be undertaken since no information is provided either on the number or choice of phenols analysed. In addition, it is not clear whether the determination of phenols includes data on octyl- and nonyl-phenols, and pentachlorophenol, which are specific phenols prescribed in the legislative frameworks identified in section 2. As discussed for toxic metals, a harmonised approach would need to be adopted across all sites, in order to undertake meaningful comparisons of the data. Generally, a non-specific method is used to determine a phenol index, which effectively provides a measure of monohydric phenols, without establishing which specific phenols are present or their individual concentrations. In view of this, comparisons of results may be inappropriate since it could not be assured that like-for-like situations were being compared.

### 9.3.3. PAHs

Whilst there are hundreds of different PAHs, only a few are are specifically prescribed in the legislation indicated in section 2. Of these, anthracene and fluoranthene are included in the WDF as indcators of more dangerous PAHs.

However, no other information is given regarding additional monitoring that might be required if these parameter was found to be present in samples.

Whether other specific PAHs should be included and monitored is a matter for debate as many PAHs possess carcinogenic properties, and are persistent in the environment. As previously discussed, a harmonised approach would need to be adopted across all sites in order to undertake meaningful comparisons of data. Both the number and specific identity of the PAHs being considered for monitoring would need to be agreed.

For example, if say the US EPA 16 PAHs are to be determined, these 16 PAHs should be clearly identified. There is little value in comparing the analysis of these 16 PAHs with the European WFD-PS-list of 6 PAHs, and then reporting both figures as "total PAH" values.

### 9.3.4. TPHs

For TPHs no single method is available that can determine all petroleum hydrocarbons in one operation. There are thousands of hydrocarbon compounds ranging from low molecular weight, simple gases and liquids to high molecular weight, complex solids. In addition, hydrocarbons can be divided into two categories, namely aliphatic hydrocarbons, and aromatic hydrocarbons (including BTEX and hundreds of PAHs). Aliphatic hydrocarbons possess joined carbon atoms, in linear and branched formations, varying in carbon lengths ranging from 2 to over a hundred. Similarly with the aromatic hydrocarbons, including the PAHs and naphthenic compounds, where the number of substitued aromatic rings ranges from 2 to 10 and above.

For any hydrocarbon determination, it is essential that the parameter determined is clearly and unambiguously defined, possibly in terms of the carbon length ranges determined. For example, hydrocarbons within the range  $C_{>10} - C_{16}$ ,  $C_{>16} - C_{21}$ ,  $C_{>21} - C_{35}$  and  $C_{>35} - C_{70}$ , with or without speciation into aliphatic and aromatic fractions. In addition, the range would need to take into account whether any "double accounting" of the hydrocarbons occurs at the end of one range and the beginning of the next range (leading to an over-estimate of the hydrocarbon concentration) or whether hydrocarons were omitted between the end of one range and the beginning of the next range (leading to an under-estimate of the hydrocarbon concentration). For reporting purposes, it is essential that the carbon length range is precisely and unambiguously defined. Typical examples for a simple range include;

- a)  $C_{>10} C_{12}$ , hydrocarbon compounds eluting after but not including  $C_{10}$  and including hydrocarbon compounds eluting up to and including  $C_{12}$ ;
- b)  $C_{>10} C_{<12}$ , hydrocarbon compounds eluting after but not including  $C_{10}$  and including hydrocarbon compounds eluting up to but not including  $C_{12}$ ;
- c)  $C_{10} C_{12}$ , hydrocarbon compounds eluting after and including  $C_{10}$  and including hydrocarbon compounds eluting up to and including  $C_{12}$ ;
- d)  $C_{10}$   $C_{<12}$ , hydrocarbon compounds eluting after and including  $C_{10}$  and including hydrocarbon compounds eluting up to but not including  $C_{12}$ ;

Without this clarity on defining exactly what is being determined, confusion will arise and it will be impossible to undertake meaningful comparisons of the respective determinations. This is irrespective of the different methods that can be used, their analytical performances, and laboratory and analyst capabilities.

Methods for the determination of hydrocarbons can involve a variety of extraction solvents, or mixtures of solvents, numerous clean-up procedures to remove interfering substances, and a choice of detection techniques to quantify the hydrocarbons. As already pointed out in section 7.3.4.2, method comparisons for this parameter are inappropriate unless identical parameters are compared on a like-for-like basis.

Consequently, for many of the methods cited in the survey, there is often little agreement in the nature of the substances being determined. A variety of methods are cited that actually determine different substances. For example, **Table 16** highlights the techniques used and the substances determined. As can be seen, the methods are very different in the respect of the substances and compounds being determined, hence there would be little point comparing the results of analyses of these methods. A like-for-like comparison cannot thus be made.

Technique	Substances determined	Comments
Matter extracted by organic solvent	All organic substances present in the sample that are soluble in the solvent and which are non-volatile when the solvent is evaporated.	This includes non-volatile TPHs and other organic substances all of which are deemed to be TPHs, and reported as such.
IR spectroscopy following extraction with a non- hydrocarbon solvent.	All substances containing carbon-hydrogen bonds.	This includes TPHs and other organic substances containing carbon-hydrogen bonds all of which are deemed to be TPHs, and reported as such.
GC-FID following extraction with organic solvent with or without clean-up, with or without fractionation into aliphatic and aromatic components.	TPHs, and possibly, other organic substances.	Depending on the clean-up procedure, organic substances may be included and reported as TPHs. The range of TPHs may depend on the extraction solvent and chromatographic conditions used.
TOC	All organic substances present in the sample.	This technique is used as a surrogate determination to estimate levels of organic contamination. All organic substances present in the sample together with TPHs are deemed to be TPHs and reported as such.

 Table 16
 Comparison of techniques used for TPH determinations

Not only are different methods used, but the methods determine different substances and groups of substances, all of which are referred to by a single term, OiW or TPHs. The fact that different methods have been used is not an issue. The

fact that different parameters are determined and compared is a fundamental issue and should not be undertaken.

### 9.3.5. Extractable substances with petroleum ether

For the parameter, extractable substances with petroleum ether, it would be unclear exactly what substances were being extracted from the sample. As well as hydrocarbon compounds being extracted, many other compounds if present in the sample, might also be extracted as well. These may include compounds such as pesticides and a wide range of other organic substances. As pointed out previously in section 9, since matrix effects might be expected to be different for different sites across Europe, there might be little agreement with the substances being extracted with petroleum ether.

In addition, petroleum ether can be obtained in several different grades depending on their boiling point fractions. The most frequently used petroleum solvent is petroleum ether 60-80, but both lower boiling point fractions and higher boiling point fractions are also commonly used. In order to carry out a meaningful comparison of the results obtained it would need to be known which grade of petroleum ether was being used in the determinations, in case differences were apparent in their extractive properties.

The monitoring of extractable substances with petroleum ether may be a good operational tool to assess the likely maximum concentration of say parameters such as OiW and TPHs.

### 9.3.6. Free cyanide

When cyanide is to be determined, the purpose of the analysis needs to be known as cyanides are referred to in three distinct forms, namely:

- (i) easily liberated cyanide (commonly referred to as free cyanide);
- (ii) complex cyanide;
- (iii) total cyanide (being defined as the sum of the easily liberated cyanide and the complex cyanide).

In practice, free or easily liberated cyanide, and total cyanide are defined by the analytical conditions under which hydrogen cyanide is liberated. Thus, changing the analytical conditions of the method used to determine cyanides may change the result obtained.

Usually, the determination of free cyanide involves dissolution of cyanide in alkali solution followed by addition of acid and then steam distillation. Under these conditions, hydrogen cyanide is liberated from, for example, simple cyanide salts, and the gas determined, normally, spectrophotometrically at a specific pH and wavelength.

Total cyanide is similarly determined, but additionally, involves the breakdown of complex cyanides salts before hydrogen cyanide gas is liberated.

Within the legislative framework (EPRTR) see **Table 1**, only hydrogen cyanide and cyanide (as total cyanide) need be monitored.

### 10. CONCLUSIONS AND FUTURE ACTIVITIES

The information provided by 100 European refineries during the CONCAWE 2012 Effluent Quality Survey has been analysed with respect to the analytical methods that were used to establish the concentrations in refinery effluents for the contaminant of concern, as included in the Water Framework Directive, the Industrial Emissions Directive and the European Pollution Release and Transfer Regulation.

One of the main findings was that for most analytes a wide range of methods were used that are either imposed by local regulators or the choice of the operator of the installation under consideration. Several of the methods in use present some challenges and require caution in drawing conclusions from the results obtained.

Rather than advocating or prescribing only those methods that could circumvent all these challenges, CONCAWE wishes that the methods are assessed on their capability to deliver useful results for the intended purpose of the measurement. Therefore, a tool has been developed to compare the different methods used for a specific analyte on the basis of a set of measurable parameters. These are the Precision or Bias, the Uncertainty of Measurement, Recovery, the Limit of Quantitation, as a function of any applicable standard (e.g. WFD EQS, IED BAT-AEL, permit ELV or operational parameter), the costs and ease of use.

Applying this tool results in a ranking of the methods as used, in the refining sector per analyte, based upon the aforementioned descriptors taken from the published standards or those reported by the laboratory using these. The rankings do not indicate, which are the better analytical methods, however these do demonstrate what methods, based upon the standard mentioned, can provide the results required to produce useful results and/or to demonstrate compliance.

Although the rankings are indicative, the actual comparison of the methods should be based on the way the standard is used in the laboratory that performs the analysis. Therefore, CONCAWE desires to upgrade the ranking tool into a webbased portal where initially its members can upload the observed performance descriptors of the respective methods in use at their laboratories.

CONCAWE hopes that this approach will generate a database that can become the basis for future identification of the better or at least fit-for-purpose methods that can be used by its members for demonstration of compliance or other purposes like operational control, effluent quality control and trend analysis. Furthermore, the information gathered in this manner night demonstrate that the methodology that is embedded in local, National or EU-wide regulations may not or no longer be the most adequate or cost effective to demonstrate compliance. Finally, this database will enable the informed debate on method improvement based upon the long experience from the analysts using these on a day-to-day basis within the refinery sector.

CONCAWE trusts that this approach will contribute to the advancement of effluent quality analysis and the subsequent use of the results obtained in a way that is scientifically sound and more objective than imposing standards, as is often the case today.

### 11. GLOSSARY

AA-EQS	annual average EQS value (to protect against long term exposure)
AA	atomic absorption
AAS	atomic absorption spectrometry
AdW	acid-digested water
AES	atomic emission spectrometry
AOX	Adsorbable organic halides
APHA	American Public Health Association (See SMEWW)
AS	Aqueous solution
AWWA	American Water Works Association (See SMEWW
BATAEL	best available technique associated emission level
BATNEEC	best available technique not entailing excessive cost
BOD	biological oxygen demand, usually over a 5-day period
BREF	best available techniques reference document
BTEX	benzene, toluene, ethyl benzene and <i>ortho-</i> , <i>meta-</i> , and <i>para-</i> xylenes
CEN	European Committee for Standardization
CFA	continuous flow analysis
CLoI	Critical level of interest
COD	chemical oxygen demand, usually over a 2-hour period
Competent authority	that organisation identified by a member state and given responsibility under various aspects of European legislation
CONCAWE	conservation of clean air and water in Europe
DoF	degrees of freedom
DVD	Digital versatile disc
DW	Drinking water
EPRTR	European Pollutant Release and Transfer Register
EQS	Environmental Quality Standard
EQSD	Environmental Quality Standards in the field of water policy Directive
ETBE	ethyl <i>tert-</i> butyl ether
EU	European Union
FIA	flow injection analysis
FID	flame ionisation detection
GF	graphite furnace
GW	Ground water
HS	Head space
ICP	inductively coupled plasma
IE	industrial effluent
IED	Industrial Emissions Directive
IPPCD	Integrated Pollution Prevention and Control Directive

IR	infra-red
ISO	International Organization for Standardization
Load	the amount of parameter, usually expressed as a mass, released into the environment over a period of time
LoD	limit of detection
LoQ	limit of quantification
L-L	liquid-liquid extraction
MAC-EQS	maximum allowable concentration (to protect against short term exposure)
MCERTS	The Environment Agency's Monitoring Certification Scheme
MEWAM	Methods for the Examination of Waters and Associated Materials See www.environment-agency.gov.uk/nls for free downloadable SCA methods
MRV	minimum reporting value
MS	mass spectrometry
MSFD	Marine Strategy Framework Directive
MTBE	methyl tert-butyl ether
OiW	oil in water
Operator	an organisation generating effluents that are discharged to the environment
PAHs	Poly-nuclear (or polycyclic) aromatic hydrocarbons
Parameter	the specific substance, compound or group of compounds analysed or determined
Performance characteristic	that feature used to assess the quality of a method, for example, its precision, bias, LoD, etc.
QA	quality assurance
QC	quality control
ReW	reagent water
RW	river water
SCA	Standing Committee of Analysts
SE	sewage effluent
SMEWW	Standard Methods for the Examination of Water and Wastewater (sometimes shortened to SM)
SS	synthetic standard
TOC	total organic carbon
TPHs	total petroleum hydrocarbons
U	Unknown
UK	United Kingdom
UoM	uncertainty of measurement
US EPA	United States Environmental Protection Agency
UV	ultra violet
WFD	Water Framework Directive
WW	waste water

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- 28. EU (2006) Directive 2006/11/EC of the European Parliament and of the Council of 15 February 2006 on pollution caused by certain dangerous substances discharged

into the aquatic environment of the Community. Official Journal of the European Union No. L64, 04.03.2006

29. EU (2008) Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending directive 2000/60/EC of the European Parliament and of the Council. Official Journal of the European Union No. L348, 24.12.2008

## APPENDIX 1 METHODS FOR PARAMETERS MENTIONED IN THE CONCAWE SURVEY

Methods indicated in red italic font are those that have not been cited in the survey but which could be used in any monitoring program that includes these parameters.

Parameter aluminium	Method	Title of method
aiummum	EN ISO 11885:1998	Water Quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP – OES)
	EN ISO 12020:2004	Water Quality – Determination of aluminium – Atomic absorption spectrometric methods
	EN ISO 15586	Water Quality – Determination of trace elements using atomic absorption spectrometry with graphite furnace
	ISO 10566	Water Quality – Determination of aluminium – Spectrometric method using pyrocatechol violet
	MEWAM 116 C	Method C, Acid soluble aluminium in marine, raw and potable waters (Second Edition) 1987, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency, 0117520403
	US EPA 200.7	Determination of metals and trace elements in water and wastes by inductively coupled plasma-atomic emission spectrometry
	US EPA 200.8	Determination of trace elements in waters and wastes by inductively coupled plasma – mass spectrometry
ammonia		
	APHA 4500	NIA – Phenate method
	APAT 4030	NIA
	ASTM	NIA – ASTM D1426-08 Standard Test Methods for Ammonia
	BS 2690	Nitrogen in Water
	D3 2090	NIA – Part 7 – Nitrile, nitrate and ammonia (free, saline and albuminoid)
	BS 6068	NIA
	C MAN 29 2003	NIA
	DIN 38406 E5	NIA – Photometric determination of the dye reaction
	EN ISO 11732	Water Quality – Determination of ammonium nitrogen – Method by
		flow analysis (CFA and FIA) and spectrometric detection
	EN ISO 11905	Water quality – Determination of nitrogen. Method using oxidative digestion with peroxodisulfate
	EN ISO 14911	Water Quality – Determination of dissolved Li+, Na+, NH4+, K+, Mn2+, Ca2+, Mg2+, Sr2+ and Ba2+ using ion chromatography – Method for water and waste water
	ET 038	NIA
	HACH 8038	NIA – Nessler method
	IRSA 4030	NIA
		Water Quality – Determination of ammonium. Distillation and titration method
	ISO 6778	Water Quality – Determination of ammonium – Potentiometric method
	ISO 7150-1	Water Quality – Determination of ammonium – Part 1 : Manual spectrometric method
	ISO 7150-2	Water Quality – Determination of ammonium – Part 2: Automated spectrometric method
	LRG004	NIA
	PE-0183	NIA

US EPA 300.7	Dissolved sodium, ammonium, potassium, magnesium and calcium in wet deposition by chemically suppressed ion chromatography
US EPA 350.2	Nitrogen, Ammonia (Colorimetric, Titrimetric, Potentiometric Distillation Procedure)
ammoniacal nitrogen	
analog 38406-E6	NIA
APAT 4030C	NIA
ASTM D1426	NIA – Standard Test Methods for Ammonia Nitrogen In Water
DEV E 5-2	NIA
DIN 38406 E5	NIA – German standard methods for the examination of water, waste water and sludge; Cations (Group E); Determination of ammonia-
	nitrogen
DO E23-1	NIA
EN ISO 11732	Water Quality – Determination of ammonium nitrogen – Method by flow analysis (CFA and FIA) and spectrometric detection
ETG01	NIA
Hach lange Test Kit	NIA
LAND 38:2000	NIA
Lange LCK 304	NIA
NBN 6604	NIA
NBN T91-252	NIA
Nessler Chemet	NIA – Direct Nesslerization method to determine ammonia
NF T90015-1	NIA
NH3NH4 ESSO	NIA
PEFQ 06 ag PC3 Ed No 3	NIA
PRR 1071	NIA
ISO 5664	Water Quality – Determination of ammonium: distillation and titration
	method
ISO 6778	Water Quality – Determination of ammonium – Potentiometric
100 0/70	method
ISO 7150-1	Water Quality – Determination of ammonium – Part 1: Manual spectrometric method
ISO 7150-2	Water Quality – Determination of ammonium – Part 2: Automated spectrometric method
SM 1426	NIA
Spectroquant Merck	NIA
US EPA 350.2	Nitrogen, Ammonia (Colorimetric, Titrimetric, Potentiometric
00 21 / 000.2	Distillation Procedure)
Anthracene	
ASTM	NIA – ASTM D4657-92(1998) Standard Test Method for Polynuclear Aromatic Hydrocarbons in Water (Withdrawn 2005)
CGM/019-a	NIA
CMO MT02	NIA
CZ-SOP-D06-03-161	NIA – Based on CSN EN ISO 6468, US EPA 8270, US EPA 8131,
02-001-000-03-101	US EPA 8091 – Determination of semi-volatile organic compounds by
	gas chromatography method with mass spectrometric detection
DIN 38407-F18	NIA – Announcement of analytical methods for sampling and testing
	in the Annex of the Prohibition of Chemicals Ordinance mentioned
	substances and substance
DIN 38407-F39	NIA – German standard methods for the examination of water, waste
	water and sludge – Jointly determinable substances (Group F) – Part
	39: Determination of selected polycyclic aromatic hydrocarbons
	(PAH) – Method using gas chromatography with mass spectrometric
	detection (GC-MS)

AOX

arsenic

EN ISO 6468	Water Quality – Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes – Gas chromatographic method after liquid-liquid extraction
EN ISO 17993	Water Quality – Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction
ISO 7981-3	Water Quality – Determination of polycyclic aromatic hydrocarbons (PAH) – Part 3: Determination of six PAH by gas chromatography with mass spectrometric detection after liquid-liquid extraction (working draft)
ISO 28540:2011	Water Quality – Determination of 16 polycyclic aromatic hydrocarbons (PAH) in water – Method using gas chromatography with mass spectrometric detection (GC-MS)'
MEWAM 165	The determination of polynuclear aromatic hydrocarbons in waters (additional methods) 1997, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
NFT90-115	NIA – Dosage de 6 hydrocarbures aromatiques polycycliques (HPLC) 1988 AFNOR
STN 75 7554	NIA – Water Quality – Determination of fluoranthene
US EPA 610	Methods for organic chemical analysis of municipal and industrial wastewater – polynuclear aromatic hydrocarbons
US EPA 3510C	Separatory funnel liquid-liquid extraction
US EPA 8100	Polynuclear aromatic hydrocarbons
US EPA 8270C	Semi-volatile organic compounds by gas chromatography/mass spectrometry (GC-MS)
US EPA 8270D	Semi-volatile organic compounds by gas chromatography/mass spectrometry (GC-MS)
US EPA 8272	Parent and alkyl polycyclic aromatics in sediment pore water by solid- phase micro-extraction and gas chromatography/mass spectrometry in selected ion monitoring mode
WAC/IV/A/002	NIA – Polycyclic aromatic hydrocarbons by GC-MS (16 of EPA)
W-PAHGMS01	NIA
EN ISO 9562	Water Quality – Determination of adsorbable organically bound halogens (AOX)
APAT 3080	NIA
APHA 3113	NIA – Metals by electrothermal atomic absorption spectrometry
ASTM D 1976	NIA – Standard test method for elements in water by inductively- coupled argon plasma atomic emission spectroscopy
ASTM D 2972-03 EN 26595	NIA – Standard test methods for arsenic in water Water Quality – Determination of total arsenic. Silver
EN ISO 11885	diethyldithiocarbamate spectrophotometric method Water Quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)
EN ISO 11969	Water Quality – Determination of arsenic – Atomic absorption spectrometric method (hydride technique)
EN ISO 15586	Water Quality – Determination of trace elements using atomic absorption spectrometry with graphite furnace
EN ISO 17294-2	Water Quality – Application of inductively coupled plasma mass spectrometry (ICP-MS) – Part 2: Determination of 62 elements
GI/PO/FQT/076	NIA
NEN 6432	NIA – Water Quality – Determiantion of arsenic by atomic absortion spectrometry – digestion with nitric and hydrochloric acid

	NFT 90-119 PEFQ52ag PC3Ed No 5 ISO 11969	NIA NIA Water Quality – Determination of arsenic – Atomic absorption spectrometric method (hydride technique)
	SM 3114B	Manual hydride generation – Atomic absorption spectrometric method
	SM 3120B SOP 4-A05/A <u>US EPA 200.7</u>	Inductively Coupled Plasma (ICP) method NIA Determination of metals and trace elements in water and wastes by inductively coupled plasma-atomic emission spectrometry
	US EPA 200.8	Determination of trace elements in waters and wastes by inductively coupled plasma – mass spectrometry
	US EPA 3005A	Acid digestion of waters for total recoverable or dissolved metals for analysis by flame AA or ICP spectroscopy
	US EPA 6010C US EPA 6020 WAC/III/B W-METMSFL1	Inductively coupled plasma-atomic emission spectrometry Inductively coupled plasma-mass spectrometry NIA NIA
benzene	APAT 5140	NIA – Solventi organici aromatici
	CGM-002-a DEV-F-9-1	NIA NIA
	DIN 38407-F9	NIA – Methods for the examination of water, waste water and sludge; substance group analysis (group F); determination of benzene and some of its derivatives by gas chromatography
	DIN 51437	NIA – Testing of benzene and benzene homologues – Determination of the non-aromatics, toluene and $C_8$ -aromatics content of benzene – Gas chromatography
	EN ISO 10301	Water Quality – Determination of highly volatile halogenated hydrocarbons – Gas-chromatographic methods
	EN ISO 15680	Water Quality – Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption
	GI/PO/FQT/164	NIA – Volatile Organic Compounds (VOC s) by Gas chromatography / mass spectrometry (GC-MS)
	ISO 11423-1	Water Quality – Determination of benzene and some derivatives – Part 1: Head-space gas chromatographic method
	ISO 11423-2	Water Quality – Determination of benzene and some derivatives – Part 2: Method using extraction and gas chromatography
	LPM4189	NIA – Determination of volatile organic components; HS / GC
	MEWAM 170	The determination of volatile organic compounds in waters and complex matrices by purge and trap or by headspace techniques 1998, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
	SOP 5-001/A US EPA 502.2	NIA Volatile organic compounds in water by purge and trap capillary column gas chromatography with photoionization and electrolytic conductivity detectors in series
	US EPA 524.2	Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry
	US EPA 602	Methods for organic chemical analysis of municipal and industrial
	US EPA 610	wastewater – purgeable aromatics Methods for organic chemical analysis of municipal and industrial wastewater – polynuclear aromatic hydrocarbons

US EPA 624	Methods for organic chemical analysis of municipal and industrial
US EPA 5021A	wastewater – purgeables Volatile organic compounds in soils and other solid matrices using
US EPA 5030 US EPA 8010 US EPA 8015B US EPA 8020 US EPA 8120 US EPA 8260	equilibrium headspace analysis Purge-and-trap for aqueous samples Halogenated volatile organics by gas chromatography Non-halogenated organics using GC/FID Aromatic volatile organics by gas chromatography Chlorinated hydrocarbons by gas chromatography Volatile organic compounds by gas chromatography/mass spectrometry (GC/MS)
US EPA 8260B	Volatile organic compounds by gas chromatography/mass spectrometry (GC/MS)
US EPA 8260C	Volatile organic compounds by gas chromatography/mass spectrometry (GC/MS)
WAC/IV/A/016 W-VOCGMS03	NIA – Headspace GC-MS NIA
benzo[b]fluoranthene	
CGM/019-a	NIA
CMO MT02 CZ-SOP-D06-03-161	NIA NIA – Based on CSN EN ISO 6468, US EPA 8270, US EPA 8131, US EPA 8091 – Determination of semi-volatile organic compounds by gas chromatography method with mass spectrometric detection
DIN 38407-F18	NIA – Announcement of analytical methods for sampling and testing in the Annex of the Prohibition of Chemicals Ordinance mentioned substances and substance
DIN 38407-F39	NIA – German standard methods for the examination of water, waste water and sludge – Jointly determinable substances (Group F) – Part 39: Determination of selected polycyclic aromatic hydrocarbons (PAH) – Method using gas chromatography with mass spectrometric detection (GC-MS)
ISO 28540:2011	Water Quality – Determination of 16 polycyclic aromatic hydrocarbons (PAH) in water – Method using gas chromatography with mass spectrometric detection (GC-MS)
ISO 17993	Water Quality – Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction
ISO WD 7981-3	Water Quality – Determination of polynuclear aromatic hydrocarbons (PAH); Part 3: Determination of six PAH in water by gas chromatography with mass spectrometric
MEWAM 165	The determination of polynuclear aromatic hydrocarbons in waters (additional methods) 1997, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
NFT90-115	NIA – Dosage de 6 hydrocarbures aromatiques polycycliques (HPLC) 1988 AFNOR
STN 75 7554	NIA – Water Quality – Determination of fluoranthene
US EPA 610	Methods for organic chemical analysis of municipal and industrial wastewater – polynuclear aromatic hydrocarbons
US EPA 3510C	Separatory funnel liquid-liquid extraction
US EPA 8100 US EPA 8270C	Polynuclear aromatic hydrocarbons Semi-volatile organic compounds by gas chromatography/mass
03 EFA 02/00	spectrometry (GC-MS)

US EPA 8270D	Semi-volatile organic compounds by gas chromatography/mass spectrometry (GC-MS)
US EPA 8275	Semi-volatile organic compounds (PAHs and PCBs)
00 EI A 02/3	in soils/sludges and solid wastes using thermal extraction/gas
	chromatography/mass spectrometry (TE/GC/MS)
WAC/IV/A/002	NIA – Polycyclic aromatic hydrocarbons by GC-MS (16 of EPA)
W-PAHGMS01	NIA
benzo[k]fluoranthene	
DIN 38407-F18	NIA – Announcement of analytical methods for sampling and testing in the Annex of the Prohibition of Chemicals Ordinance mentioned substances and substance
ISO 17993	Water Quality – Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction
ISO 28540:2011	Water Quality – Determination of 16 polycyclic aromatic
	hydrocarbons (PAH) in water – Method using gas chromatography
	with mass spectrometric detection (GC-MS)
ISO WD 7981-3	Water Quality – Determination of polynuclear aromatic hydrocarbons (PAH); Part 3: Determination of six PAH in water by gas chromatography with mass spectrometric
MEWAM 165	The determination of polynuclear aromatic hydrocarbons in waters
	(additional methods) 1997, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
NFT90-115	NIA – Dosage de 6 hydrocarbures aromatiques polycycliques (HPLC) 1988 AFNOR
US EPA 610	Methods for organic chemical analysis of municipal and industrial
	wastewater – polynuclear aromatic hydrocarbons
US EPA 3510C	Separatory funnel liquid-liquid extraction
US EPA 8100	Polynuclear aromatic hydrocarbons
US EPA 8270D	Semi-volatile organic compounds by gas chromatography/mass spectrometry (GC-MS)
WAC/IV/A/002	NIA – Polycyclic aromatic hydrocarbons by GC-MS (16 of EPA)
W-PAHGMS01	NIA
benzo[ <i>g,h,i</i> ]perylene	
CGM/019-a	NIA
CMO MT02	NIA Deced on CON ENLIGO CACO, LIC EDA 0070, LIC EDA 0424
CZ-SOP-D06-03-161	NIA – Based on CSN EN ISO 6468, US EPA 8270, US EPA 8131, US EPA 8091 – Determination of semi-volatile organic compounds by gas chromatography method with mass spectrometric detection
DIN 38407-F18	NIA – Announcement of analytical methods for sampling and testing in the Annex of the Prohibition of Chemicals Ordinance mentioned substances and substance
DIN 38407-F39	NIA – German standard methods for the examination of water, waste water and sludge – Jointly determinable substances (Group F) – Part
	39: Determination of selected polycyclic aromatic hydrocarbons (PAH) – Method using gas chromatography with mass spectrometric detection (GC-MS)
ISO 28540:2011	Water Quality – Determination of 16 polycyclic aromatic hydrocarbons (PAH) in water – Method using gas chromatography
	with mass spectrometric detection (GC-MS)
ISO 17993	Water Quality – Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction

ISO WD 7981-3	Water Quality – Determination of polynuclear aromatic hydrocarbons (PAH); Part 3: Determination of six PAH in water by gas
	chromatography with mass spectrometric
MEWAM 165	The determination of polynuclear aromatic hydrocarbons in waters
	(additional methods) 1997, Standing Committee of Analysts, Methods
	for the Examination of Waters and Associated Materials, Environment Agency
NFT90-115	NIA – Dosage de 6 hydrocarbures aromatiques polycycliques (HPLC) 1988 AFNOR
STN 75 7554	NIA – Water Quality – Determination of fluoranthene
US EPA 610	Methods for organic chemical analysis of municipal and industrial wastewater – polynuclear aromatic hydrocarbons
US EPA 3510C	Separatory funnel liquid-liquid extraction
US EPA 8100	Polynuclear aromatic hydrocarbons
US EPA 8270D	Semi-volatile organic compounds by gas chromatography/mass spectrometry (GC-MS)
US EPA 8277	NIA
WAC/IV/A/002	NIA – Polycyclic aromatic hydrocarbons by GC-MS (16 of EPA)
W-PAHGMS01 benzo[a]pyrene	NIA
CGM/019-a	NIA
CMO MT02	NIA
CZ-SOP-D06-03-161	NIA – Based on CSN EN ISO 6468, US EPA 8270, US EPA 8131,
	US EPA 8091 – Determination of semi-volatile organic compounds by
	gas chromatography method with mass spectrometric detection
DIN 38407-F18	NIA – Announcement of analytical methods for sampling and testing in the Annex of the Prohibition of Chemicals Ordinance mentioned
	substances and substance
DIN 38407-F39	NIA – German standard methods for the examination of water, waste
	water and sludge – Jointly determinable substances (Group F) – Part
	39: Determination of selected polycyclic aromatic hydrocarbons
	(PAH) – Method using gas chromatography with mass spectrometric
ISO 28540:2011	detection (GC-MS) Water Quality – Determination of 16 polycyclic aromatic
100 20040.2011	hydrocarbons (PAH) in water – Method using gas chromatography
	with mass spectrometric detection (GC-MS)
ISO 17993	Water Quality – Determination of 15 polycyclic aromatic
	hydrocarbons (PAH) in water by HPLC with fluorescence detection
ISO WD 7981-3	after liquid-liquid extraction Water Quality – Determination of polynuclear aromatic hydrocarbons
130 WD 7981-3	(PAH); Part 3: Determination of six PAH in water by gas
	chromatography with mass spectrometric
MEWAM 165	The determination of polynuclear aromatic hydrocarbons in waters
	(additional methods) 1997, Standing Committee of Analysts, Methods
	for the Examination of Waters and Associated Materials, Environment
NFT90-115	Agency
NF190-115	NIA – Dosage de 6 hydrocarbures aromatiques polycycliques (HPLC) 1988 AFNOR
STN 75 7554	NIA – Water Quality – Determination of fluoranthene
US EPA 610	Methods for organic chemical analysis of municipal and industrial
US EPA 3510C	wastewater – polynuclear aromatic hydrocarbons Separatory funnel liquid-liquid extraction
US EPA 8100	Polynuclear aromatic hydrocarbons
US EPA 8270C	Semi-volatile organic compounds by gas chromatography/mass
	spectrometry (GC-MS)

	US EPA 8270D	5 1 55 515
		spectrometry (GC-MS)
	US EPA 8274	NIA
	WAC/IV/A/002	NIA – Polycyclic aromatic hydrocarbons by GC-MS (16 of EPA)
	W-PAHGMS01	NIA
BOD		NUA
	APAT 5120 B	NIA E day BOD test
	AWWA 5210B	5-day BOD test
	DIN 38402	NIA NIA - Determination of Discharging Common Demand (DOD)
	DIN 38409	NIA – Determination of Biochemical Oxygen Demand (BOD)
	EN 1483	Water Quality – Determination of mercury Method using atomic
		absorption spectrometry
	EN 1899-1	Water Quality – Determination of biochemical oxygen demand after n
		days (BODn) – Part 1: Dilution and seeding method with allylthiourea
		addition
	EN 1899-2	Water Quality – Determination of biochemical oxygen demand after n
		days (BODn) – Part 2: Method for undiluted samples
	EN 25813	Water Quality – Determination of dissolved oxygen – lodometric
		method
	EN ISO 5813	Water Quality – Determination of dissolved oxygen – Iodometric
		method
	EN ISO 5815	Water Quality – Determination of biochemical oxygen demand after n
		days (BODn) – Part 1: Dilution and seeding method with allylthiourea
		addition
	ET066	NIA
	LAND 47-1/2:2007	NIA
	M1094 (2008)	NIA
	NFT 90 103	NIA
	MN/001-a	NIA
	MPI 065	NIA
	NBN 407	NIA
PEFQ3	36 ag PC3 Ed No 4	NIA
	US EPA 405.1	Biochemical Oxygen Demand (5 Days, 20°C)
	WAC/III/D	NIA
BTEX		
	ISO 11423-1	Water Quality – Determination of benzene and some derivatives –
		Part 1: Head-space gas chromatographic method
	US EPA 3810	Headspace
	US EPA 8020	aromatic volatile organics by gas chromatography
cadmium		NUA
	APAT 3120B	NIA
	BS 6964	NIA
	DO-E22-1	NIA
	DS 259	NIA – Water Quality – Determination of metals in water, soil, sludge and sediments – General principles and guidelines for determination
		by atomic absorption spectrophotometry in flame
	EN ISO 5961	Water Quality – Determination of cadmium by atomic absorption
	LIN 130 3301	spectrometry
	ISO 8288-1	
	130 0200-1	Water Quality – Determination of cobalt, nickel, copper, zinc, cadmium and lead – Flame atomic absorption spectrometric methods
	EN ISO 11885	Water Quality – Determination of selected elements by inductively
	EN 130 11003	coupled plasma optical emission spectrometry (ICP-OES)
	ISO 15586	Water Quality – Determination of trace elements using atomic
	130 13360	absorption spectrometry with graphite furnace
		absorption spectrometry with graphite turnate

chloride

ISO 17294	Water Quality – Application of inductively coupled plasma mass spectrometry (ICP-MS) – Part 2 – Determination of 62 elements
MEWAM 163 B	Inductively coupled plasma spectrometry 1996, Method B, Standing
IVIL VAIVI 105 D	Committee of Analysts, Methods for the Examination of Waters and
	Associated Materials, Environment Agency
NEN 6966	NIA – Environment – Analysis of selected elements in water, eluates
	and destruaten – atomic emission spectrometry with inductively
	coupled plasma
SM 3120B	Inductively Coupled Plasma (ICP) method
SMEWW 3111B	Metals by flame atomic absorption spectrometry
US EPA 200.7	Determination of metals and trace elements in water and wastes by
	inductively coupled plasma-atomic emission spectrometry
US EPA 200.8	Determination of trace elements in waters and wastes by inductively
	coupled plasma – mass spectrometry
US EPA 3005A	Acid digestion of waters for total recoverable or dissolved metals for
	analysis by flame AA or ICP spectroscopy
US EPA 6010	Inductively coupled plasma-atomic emission spectrometry
US EPA 6020	Inductively coupled plasma-mass spectrometry
WAC/III/B	NIA
W-METMSFL1	NIA
APAT 4020	NIA
APHA 4500	NIA
ASTM D 512B	NIA – Standard test methods for chloride ion in water
BS 6676	NIA
DIN 38406	NIA
DO-D20-1	NIA
GI/PO/FQT/118	NIA Water Quality Method for the determination of chloride via a silver
ISO 9297	Water Quality – Method for the determination of chloride via a silver nitrate titration with chromate indicator (Mohr's method)
ISO 10304-1	Water Quality – Determination of dissolved anions by liquid
150 10504-1	chromatography of ions – Part 1: Determination of bromide, chloride,
	fluoride, nitrate, nitrite, phosphate and sulfate
ISO 10304-2	Water Quality – Determination of dissolved anions by liquid
	chromatography of ions. Part 2 – Determination of bromide, chloride,
	nitrate, nitrite, orthophosphate and 69hysic69e in waste water
ISO 15682	Water Quality – Determination of chloride by flow analysis (CFA and
	FIA) and photometric or potentiometric detection
ISBN 1175123313	NIA
LAND 63:2004	NIA
NEN 6476	NIA – Water Quality – Determination of the content of chloride by
	potentiometric titration
NEN 6604	NIA – Water Quality – Determination of the concentration of
	ammonium, nitrate, nitrite, chloride, ortho-phosphate, sulphate and
	silicate with a discrete analysis and spectrophotometric detection
TOTAL 798	NIA
UNE 77042	NIA – Water Quality – Chloride determination – Potentiometric
	method
UOP 456	NIA Determination of increasing anions in drinking water by ion
US EPA 300.1	Determination of inorganic anions in drinking water by ion
	chromatography
US EPA 9056 WAC/III/C	Determination of inorganic anions by ion chromatography NIA
WAC/III/C W-CL-IC	NIA
VV-OL-IO	

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## chromium

Chioman	
APAT 3150	NIA
ASTMD 1976	NIA – Standard test method for elements in water by inductively-
	coupled argon plasma atomic emission spectroscopy
EN 1233	Water Quality – Determination of chromium. Atomic absorption
	spectrometric methods
EN ISO 11885	Water Quality – Determination of selected elements by inductively
LN 150 11005	
	coupled plasma optical emission spectrometry (ICP-OES)
EN ISO 15586	Water Quality – Determination of trace elements using atomic
	absorption spectrometry with graphite furnace
DO-E22-1	NIA
GI/PO/FQT/068	NIA
HACH 8024	NIA
MEWAM 163 B	Inductively coupled plasma spectrometry 1996, Method B, Standing
	Committee of Analysts, Methods for the Examination of Waters and
	Associated Materials, Environment Agency
ISO 9174	Water Quality – Determination of chromium – Atomic absorption
	spectrometric methods
ISO 17294	Water Quality – Application of inductively coupled plasma mass
100 11201	spectrometry (ICP-MS) – Part 2 – Determination of 62 elements
NEN 6966	NIA – Environment – Analysis of selected elements in water, eluates
	and destruaten – atomic emission spectrometry with inductively
	coupled plasma
DN 77/0 04004/00	
PN-77/C-04604/02	NIA
SM 3120B	Inductively Coupled Plasma (ICP) method
SMEWW 3111B	Metals by flame atomic absorption spectrometry
SOP 4-A04/A	NIA
US EPA 200.7	Determination of metals and trace elements in water and wastes by
	inductively coupled plasma-atomic emission spectrometry
US EPA 200.8	Determination of trace elements in waters and wastes by inductively
	coupled plasma – mass spectrometry
US EPA 3005A	Acid digestion of waters for total recoverable or dissolved metals for
	analysis by flame AA or ICP spectroscopy
US EPA 6010C	Inductively coupled plasma-atomic emission spectrometry
US EPA 6020	Inductively coupled plasma-mass spectrometry
WAC/IIIB	NIA
W-METMSFL1	NIA
chromium (VI)	
APAT 3150C	NIA
APHA 3500	
EA/006a	NIA
EN ISO 18412	Water Quality – Determination of chromium (VI). Photometric method
	for weakly contaminated water
EN ISO 23913	Water Quality – Determination of chromium (VI). Method using flow
	analysis (FIA and CFA) and spectrometric detection
HACH 8023	NIA
ISO 11083	Water Quality – Determination of chromium(VI) – Spectrometric
	method using 1,5-diphenylcarbazide
ISO 11885	Water Quality – Determination of selected elements by inductively
	coupled plasma optical emission spectrometry (ICP-OES)
NF T90-043	NIA
PN-77/C-04604/08	NIA
UNE 77-061-89	NIA – Methods of analysis of industrial waste water: determination of
0.12 001 00	chromium: diphenylcarbazide method
	งกางกาณกา. แตกอาญเงลามิลิ่มเนอ กาอแกบน

US EPA 200.7	Determination of metals and trace elements in water and wastes by
US EPA 200.8	<i>inductively coupled plasma-atomic emission spectrometry</i> Determination of trace elements in waters and wastes by inductively
WAC/III/B cobalt	coupled plasma – mass spectrometry NIA
APHA 3113 EN ISO 11885	Metals by electrothermal atomic absorption spectrometry Water Quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)
ISO 15586	Water Quality – Determination of trace elements using atomic absorption spectrometry with graphite furnace
ISO 17294	Water Quality – Application of inductively coupled plasma mass spectrometry (ICP-MS) – Part 2: Determination of 62 elements
MEWAM 163 B	Inductively coupled plasma spectrometry 1996, Method B, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
US EPA 200.7	
US EPA 200.8	Determination of trace elements in waters and wastes by inductively coupled plasma – mass spectrometry
US EPA 6020A WAC/III/B	Inductively coupled plasma-mass spectrometry NIA
W-METMSFL2	NIA
COD APAT 5130	NIA
APAT 5130 APHA 5220 B	NIA
ASTM 1252	
A31W1232	NIA – Standard test methods for chemical oxygen demand (dichromate oxygen demand) of water
ASTM 5220 D	NIA
DIN 38409	NIA
EA/011-a	NIA
ET067	NIA
ISO 6060	Water Quality – Determination of the chemical oxygen demand
ISO 15705	Water Quality – Determination of the chemical oxygen demand index (ST-COD) – Small-scale sealed-tube method
HACH 8000	NIA
HACH LANGE LCK 14114314	NIA
LAND 83:2006	NIA
MEWAM 215	The determination of chemical oxygen demand in waters and effluents (2007) Standing Committee of Analysts, Methods for the
	Examination of Waters and Associated Materials, Environment Agency
NBN T91-201	NIA
NFT 90 101	NIA
PE-0182	NIA
STN 75 7376	NIA – Water Quality – Determination of chemical oxygen
	demand.
TNV 757520/A UNE 77004	NIA NIA – Determination of Biochemical Oxygen Demand (BOD)
US EPA 410.4	Dichromate method The determination of chemical oxygen demand by semi-automated
WAC/III/D	colorimetry NIA

# copper

copper	
APAT 3250 B	NIA
APHA 3113	Metals by electrothermal atomic absorption spectrometry
ASTM 1688-07	NIA – Standard test methods for copper in water
ASTM D 1976	NIA – Standard test method for elements in water by inductively-
ASTIM D 1970	
	coupled argon plasma atomic emission spectroscopy
EN ISO 11885	Water Quality – Determination of selected elements by inductively
	coupled plasma optical emission spectrometry (ICP – OES)
EN ISO 15586	Water Quality – Determination of trace elements using atomic
	absorption spectrometry with graphite furnace
DO-E22-1	NIA
DS 259	NIA – Water Quality – Determination of metals in water, soil, sludge
D3 239	
	and sediments – General principles and guidelines for determination
	by atomic absorption spectrophotometry in flame
GI/PO/FQT/068	NIA
MEWAM 163 B	Inductively coupled plasma spectrometry 1996, Method B, Standing
	Committee of Analysts, Methods for the Examination of Waters and
	Associated Materials, Environment Agency
NEN 6966	NIA – Environment – Analysis of selected elements in water, eluates
NEN 0500	
	and destruaten – atomic emission spectrometry with inductively
	coupled plasma
PEFQ12 ag PC3 Ed No 1	NIA
ISO 8288	Water Quality – Determination of cobalt, nickel, copper, zinc,
	cadmium and lead – Flame atomic absorption spectrometric methods
ISO 17294	Water Quality – Application of inductively coupled plasma mass
	spectrometry (ICP-MS) – Part 2: Determination of 62 elements
IT-A-018C	NIA
SM 3120B	Inductively Coupled Plasma (ICP) method
SOP 4-A03/A	NIA
US EPA 200.7	Determination of metals and trace elements in water and wastes by
	inductively coupled plasma-atomic emission spectrometry
US EPA 200.8	Determination of trace elements in waters and wastes by inductively
	coupled plasma – mass spectrometry
US EPA 3005	Acid digestion of waters for total recoverable or dissolved metals for
	analysis by flaa or icp spectroscopy
US EPA 6010	Inductively coupled plasma-atomic emission spectrometry
US EPA 6020	Inductively coupled plasma-mass spectrometry
WAC/III/B	NIA
W-METMSFL2	NIA
dichloromethane	
CGM/002-a	NIA
EN ISO 10301	Water Quality – Determination of highly volatile halogenated
	hydrocarbons. Gas-chromatographic methods
EN ISO 15680	Water Quality – Gas-chromatographic determination of a number of
	monocyclic aromatic hydrocarbons, naphthalene and several
	chlorinated compounds using purge-and-trap and thermal desorption
MEWAM 170	The determination of volatile organic compounds in waters and
	complex matrices by purge and trap or by headspace techniques
	1998, Standing Committee of Analysts, Methods for the Examination
	of Waters and Associated Materials, Environment Agency
US EPA 524	Measurement of purgeable organic compounds in water by capillary
	column gas chromatography/mass spectrometry
US EPA 624	Methods for organic chemical analysis of municipal and industrial
03 EFA 024	
	wastewater – purgeables
US EPA 3510C	Separatory funnel liquid-liquid extraction

US EPA 5030C US EPA 8010 US EPA 8100 US EPA 8020 <i>US EPA 8260</i> US EPA 8270D	Purge-and-trap for aqueous samples Halogenated volatile organics by gas chromatography Polynuclear aromatic hydrocarbons Aromatic volatile organics by gas chromatography <i>Volatile organic compounds by gas chromatography/mass</i> <i>spectrometry (GC/MS)</i> Semi-volatile organic compounds by gas chromatography/mass spectrometry (GC-MS)
ethylbenzene APAT 5140	NIA
DEV-F-9-1 DIN 38407-F9	NIA NIA
EN ISO 11423-1	Water Quality – Determination of benzene and some derivatives – Part 1: Head-space gas chromatographic method
EN ISO 15680	Water Quality – Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption
LPM 4189	NIA – Determination of volatile organic components; HS / GC
MEWAM 170	The determination of volatile organic compounds in waters and complex matrices by purge and trap or by headspace techniques 1998, Standing Committee of Analysts, Methods for the Examination
	of Waters and Associated Materials, Environment Agency
EA-NLS	
US EPA 502.0	Volatile organic compounds in water by purge and trap capillary column gas chromatography with photoionization and electrolytic conductivity detectors in series
US EPA 524	Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry
US EPA 542	Determination of 86 Volatile Organic Compounds in Water by Gas Chromatography/Mass Spectrometry
US EPA 602	Methods for organic chemical analysis of municipal and industrial wastewater – purgeable aromatics
US EPA 610	Methods for organic chemical analysis of municipal and industrial wastewater – polynuclear aromatic hydrocarbons
US EPA 624	Methods for organic chemical analysis of municipal and industrial wastewater – purgeables
US EPA 5021	Volatile organic compounds in soils and other solid matrices using equilibrium headspace analysis
US EPA 5030C	Purge-and-trap for aqueous samples
US EPA 8010	Halogenated volatile organics by gas chromatography
US EPA 8015B	Non-halogenated organics using GC/FID
US EPA 8020	Aromatic volatile organics by gas chromatography
US EPA 8022	NIA
US EPA 8120 US EPA 8260	Chlorinated hydrocarbons by gas chromatography Volatile organic compounds by gas chromatography/mass
WAC/IV/A/016	spectrometry (GC/MS) NIA – Headspace GC-MS
W-VOCGMS03	NIA
extractable substances with	
petroleum ether	
SR 7587:1996	NIA Mineral oils
Fluoranthene CGM/019-a CMO MT02	NIA NIA

CZ-SOP-D06-03-161	NIA – Based on CSN EN ISO 6468, US EPA 8270, US EPA 8131, US EPA 8091 – Determination of semi-volatile organic compounds by
DIN 38407-F18	gas chromatography method with mass spectrometric detection NIA – Announcement of analytical methods for sampling and testing in the Annex of the Prohibition of Chemicals Ordinance mentioned
	substances and substance
DIN 38407-F39	NIA – German standard methods for the examination of water, waste
	water and sludge – Jointly determinable substances (Group F) – Part 39: Determination of selected polycyclic aromatic hydrocarbons (PAH) – Method using gas chromatography with mass spectrometric detection (GC-MS)
EN ISO 6468	Water Quality – Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes. Gas chromatographic method after liquid-liquid extraction
ISO 28540:2011	Water Quality – Determination of 16 polycyclic aromatic hydrocarbons (PAH) in water – Method using gas chromatography with mass spectrometric detection (GC-MS)
ISO 17993	Water Quality – Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction
ISO WD 7981-3	Water Quality – Determination of polynuclear aromatic hydrocarbons (PAH); Part 3: Determination of six PAH in water by gas
	chromatography with mass spectrometric
MEWAM 165	The determination of polynuclear aromatic hydrocarbons in waters (additional methods) 1997, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment
NFT90-115	Agency NIA – Dosage de 6 hydrocarbures aromatiques polycycliques (HPLC) 1988 AFNOR
STN 75 7554	NIA – Water Quality – Determination of fluoranthene
US EPA 610	Methods for organic chemical analysis of municipal and industrial wastewater – polynuclear aromatic hydrocarbons
US EPA 3510C	Separatory funnel liquid-liquid extraction
US EPA 8100	Polynuclear aromatic hydrocarbons
US EPA 8270D US EPA 8273	Semi-volatile organic compounds by gas chromatography/mass spectrometry (GC-MS) NIA
WAC/IV/A/002	NIA – Polycyclic aromatic hydrocarbons by GC-MS (16 of EPA)
W-PAHGMS01	NIA
APAT 4020	NIA
AWWA 4500	Fluoride
D06-02-068	NIA
DIN 38405	NIA
EN ISO 10304	Water Quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate
ES/002a	NIA
ISO 10359-1	Water Quality – Determination of fluoride – Part 1: Electrochemical probe method for potable and lightly polluted water
ISO 10359-2	Water Quality – Determination of fluoride – Part 2: Determination of inorganically bound total fluoride after digestion and distillation
NEN 6589	NIA – Water – Potentiometric determination of the content of total inorganic fluoride with flow systems (FIA and CFA)
NF T90-004	NIA

fluoride

300.0 340.1	NIA Determination of inorganic anions by ion chromatrography Fluoride, Total (Colorimetric, SPADNS with Bellack Distillation)
9056	Determination of Inorgainic Anions by Ion Chromatography NIA
2036 4500 3-2-3 8405 8406 /019a 4403 8027 6703	NIA NIA – Standard test methods for cyanides in water Cyanide NIA NIA NIA NIA Water Quality – Determination of total cyanide and free cyanide by continuous flow analysis NIA Water Quality – Determination of cyanide – Part 2: Determination of easily liberatable cyanide The determination of cyanide and thiocyanate in soils and similar
60-30 7415 12251	matrices (2011) NIA NIA NIA – Qualità dell'acqua: determinazione dei cianuri liberi e totali – Metodo mediante decomposizione dei cianocomplessi, distillazione e misura finale con: test in 75hysic75, cromatografia ionica, flow injection (FIA) NIA – Available cyanide in water
C/III/D	NIA
110 0	NIA
MT02	NIA
	NIA – Based on CSN EN ISO 6468, US EPA 8270, US EPA 8131, US EPA 8091 – Determination of semi-volatile organic compounds by gas chromatography method with mass spectrometric detection
	NIA – Announcement of analytical methods for sampling and testing in the Annex of the Prohibition of Chemicals Ordinance mentioned substances and substance
7-F39	NIA – German standard methods for the examination of water, waste water and sludge – Jointly determinable substances (Group F) – Part 39: Determination of selected polycyclic aromatic hydrocarbons (PAH) – Method using gas chromatography with mass spectrometric detection (GC-MS)
:2011	Water Quality – Determination of 16 polycyclic aromatic hydrocarbons (PAH) in water – Method using gas chromatography with mass spectrometric detection (GC-MS)
7993	Water Quality – Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction
	300.0 340.1 9056 //II/C 4070 2036 4500 3-2-3 8405 8406 019a 4403 8027 6703 / 235 60-30 7415 2251 1677 //II/D 019-a 4702 3-161 7-F18 7-F39 22011 7993

## indeno[1,2,3-cd]pyrene

(continued)

ISO WD 7981-3 Water Quality – Determination of polynuclear aromatic hydrocarbons (PAH); Part 3: Determination of six PAH in water by gas chromatography with mass spectrometric

MEWAM 165	The determination of polynuclear aromatic hydrocarbons in waters (additional methods) 1997, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
NFT90-115	NIA – Dosage de 6 hydrocarbures aromatiques polycycliques (HPLC) 1988 AFNOR
STN 75 7554	NIA – Water Quality – Determination of fluoranthene
US EPA 610	Methods for organic chemical analysis of municipal and industrial wastewater – polynuclear aromatic hydrocarbons
US EPA 3510C	Separatory funnel liquid-liquid extraction
US EPA 8100	Polynuclear aromatic hydrocarbons
US EPA 8270C	Semi-volatile organic compounds by gas chromatography/mass spectrometry (GC-MS)
US EPA 8270D	Semi-volatile organic compounds by gas chromatography/mass spectrometry (GC-MS)
US EPA 8278	NIA
WAC/IV/A/002	NIA – Polycyclic aromatic hydrocarbons by GC-MS (16 of EPA)
W-PAHGMS01	NIA
APAT 3160	NIA
APHA 3113	Metals by electrothermal atomic absorption spectrometry
APHA 3500	Iron
EN ISO 11885	Water Quality – Determination of selected elements by inductively
	coupled plasma optical emission spectrometry (ICP – OES)
EN ISO 15586	Water Quality – Determination of trace elements using atomic
EN 180 19900	absorption spectrometry with graphite furnace
EN ISO 17294-2	Water Quality – Application of inductively coupled plasma mass
LN 150 17294-2	spectrometry (ICP-MS) – Part 2: Determination of 62 elements
FDT 90-112	NIA
HACH 8147	NIA Mater Quality – Data mination of income Construction mathematics
ISO 6332	Water Quality – Determination of iron – Spectrometric method using 1,10-phenanthroline
MEWAM 76	Iron and Manganese in Potable Waters by Atomic Absorption Spectrophotometry 1983, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
NFT90-017	NIA
PEFQ12 ag PC3 Ed No 1	NIA
SR 13315:1996	NIA
US EPA 200.7	Determination of metals and trace elements in water and wastes by inductively coupled plasma-atomic emission spectrometry
US EPA 236.2	Iron (AA, furnace technique)
US EPA 3005	Acid digestion of waters for total recoverable or
	dissolved metals for analysis by flame AA or ICP spectroscopy
US EPA 6010	Inductively coupled plasma-atomic emission spectrometry
US EPA 6020	Inductively coupled plasma-mass spectrometry
WAC/III/B	NIA
l nitrogen	
APAT 5030	NIA
EN 25663	Water Quality – Determiantion of Kjeldahl nitrogen - method after mineralisation with selenium.
ETG 19	NIA
HACH 8075	NIA

Kjeldahl

iron

MEWAM 126 B	Methods for the Examination of Waters and Associated Materials,
NEN 6641	Environment Agency, ISBN 0117521299 NIA – Sludge – Determination of the sum of the levels of ammonium nitrogen and organic nitrogen after Kjeldahl mineralization with
NEN 6646	selenium NIA – Water – Spectrophotometric determination of the content of ammoniacal nitrogen and of the sum of the contents of ammoniacal nitrogen and organically bound nitrogen according to Kjeldahl by means of a continuous flow analysis
ISO 5663	Water Quality – Determination of Kjeldahl nitrogen – Method after mineralization with selenium
VL/007-a	NIA
WAC/III/D	NIA
W-NKL-PHO	NIA
APAT 3230B	NIA
DIN 38406-E6	NIA – German standard methods for the examination of water, waste water and sludge – Cations (Group E) – Part 6: Determination of lead by atomic absorption spectrometry (AAS) (E6)
DO-E22-1	NIA
DS 259-ICP	NIA – Water Quality – Determination of metals in water, soil, sludge and sediments – General principles and guidelines for determination by atomic absorption spectrophotometry in flame
EN ISO 11885	Water Quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP – OES)
EN ISO 15586	Water Quality – Determination of trace elements using atomic absorption spectrometry with graphite furnace
GI/PO/FQT/068	NIA
HACH 8033	NIA
ISO 8288-1	Water Quality – Determination of cobalt, nickel, copper, zinc,
ISO 17294	cadmium and lead – Flame atomic absorption spectrometric methods Water Quality – Application of inductively coupled plasma mass spectrometry (ICP-MS) – Part 2 – Determination of 62 elements
LW 1089	NIA
MEWAM 163 B	Inductively coupled plasma spectrometry 1996, Method B, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
NEN 6966	NIA – Environment – Analysis of selected elements in water, eluates and destruaten – atomic emission spectrometry with inductively coupled plasma
NFT 90-112	NIA
SM 3120B	Inductively Coupled Plasma (ICP) method
US EPA 200.7	Determination of metals and trace elements in water and wastes by inductively coupled plasma-atomic emission spectrometry
US EPA 200.8	Determination of trace elements in waters and wastes by inductively coupled plasma – mass spectrometry
US EPA 3005A	Acid digestion of waters for total recoverable or dissolved metals for analysis by flame AA or ICP spectroscopy
US EPA 6010C	Inductively coupled plasma-atomic emission spectrometry
US EPA 6020	Inductively coupled plasma-atomic emission spectrometry
WAC/III/B	NIA
W-METMSFL1	NIA

lead

#### manganese

EN ISO 1	885 Water Quality – Determination of selected elements by inducti coupled plasma optical emission spectrometry (ICP – OES)	vely
EN ISO 1		1
EN ISO 1	294 Water Quality – Application of inductively coupled plasma ma	
MEWA	<ul> <li>spectrometry (ICP-MS) – Part 2: Determination of 62 element.</li> <li>Iron and Manganese in Potable Waters by Atomic Absorption Spectrophotometry 1983, Standing Committee of Analysts, Mathematical Science (1998)</li> </ul>	
	the Examination of Waters and Associated Materials, Environ Agency, ISBN 0117517275	
MEWAN	163 Inductively Coupled Plasma Spectrometry 1996 Standing Con Analysts, Methods for the Examination of Waters and Associa Materials, Environment Agency, ISBN 0117532444	
US EPA :		tes by
US EPA :		ctively
mercury		
APAT 3 BS EN		nic
	absorption spectrometry	
BS EN 2 CSN 75		
001173	amalgamation and atomic absorption	
DO-E		
EN ISO 1	338 Water Quality – Determination of mercury. Enrichment method amalgamation	ds by
EN 1	506 Water Quality – Determination of mercury by atomic fluoresce spectrometry	nce
EN ISO 1		vely
EN ISO 1	846 Water Quality – Determination of mercury. Method using atom absorption spectrometry (AAS) with and without enrichment	nic
GI/PO/FQ		
ISO 1	in water – Part 2: Nitric acid digestion	
ISO 1	spectrometry (ICP-MS) – Part 2: Determination of 62 elements	S
ISO 1	fluorescence spectrometry	mic
ROG		
STN 83 05 US EPA :		tes by
US EPA 3		als for
US EPA 6 US EPA 6	IOC Inductively coupled plasma-atomic emission spectrometry	
МТВЕ		
DIN 3840	water and sludge; substance group analysis (Group F); detern	nination
EN ISO 114	of benzene and some of its derivatives by gas chromatograph 3-1 Water Quality – Determination of benzene and some derivativ Part 1: Head-space gas chromatographic method	

LPM 4189 <i>MEWAM 170</i>	NIA – Determination of volatile organic components; HS / GC The determination of volatile organic compounds in waters and complex matrices by purge and trap or by headspace techniques 1998, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
EA-NLS FFP	
EA-NLS MCERTS	
US EPA 524.2	Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry
US EPA 602	Methods for organic chemical analysis of municipal and industrial wastewater – purgeable aromatics
US EPA 610	Methods for organic chemical analysis of municipal and industrial wastewater – polynuclear aromatic hydrocarbons
US EPA 624	Methods for organic chemical analysis of municipal and industrial wastewater – purgeables
US EPA 5021A	Volatile organic compounds in soils and other solid matrices using equilibrium headspace analysis
US EPA 8020	Aromatic volatile organics by gas chromatography
US EPA 8120	Chlorinated hydrocarbons by gas chromatography
US EPA 8260	Volatile organic compounds by gas chromatography/mass spectrometry (GC/MS)
WAC/IV/A/016	Headspace GC-MS
W-VOCGMS03	NIA
MTBE + ETBE see MTBE above	
naphthalene	
CMO-MT02 CZ-SOP-D06-03-161	NIA - NIA – Based on CSN EN ISO 6468, US EPA 8270, US EPA 8131,
DIN 38407-F18	US EPA 8091 – Determination of semi-volatile organic compounds by gas chromatography method with mass spectrometric detection NIA – German standard methods for the examination of water, waste water, and sludge – Jointly determinable substances (group F) – Part 18: Determination of 15 polycyclic aromatic hydrocarbons (PAH) by high performance liquid chromatography (HPLC) with fluorescence
DIN 38407-F39	detection (F 18) NIA – German standard methods for the examination of water, waste water and sludge – Jointly determinable substances (group F) – Part 39: Determination of selected polycyclic aromatic hydrocarbons (PAH) – Method using gas chromatography with mass spectrometric
ISO 28540:2011	detection (GC-MS) (F 39) Water Quality – Determination of 16 polycyclic aromatic hydrocarbons (PAH) in water – Method using gas chromatography
ISO 6468	with mass spectrometric detection (GC-MS) Water Quality – Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes – Gas
ISO 15680	chromatographic method after liquid-liquid extraction Water Quality – Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several
ISO 17993	chlorinated compounds using purge-and-trap and thermal desorption Water Quality – Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction
NFT 90-115	NIA

	MEWAM 165	The determination of polynuclear aromatic hydrocarbons in waters (additional methods) 1997, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
	STN 75 7554 <u>US EPA 524.2</u>	NIA – Water Quality – Determination of fluoranthene Measurement of purgeable organic compounds in water by capillary
	US EPA 610	column gas chromatography/mass spectrometry Methods for organic chemical analysis of municipal and industrial
	US EPA 3510C US EPA 8100	wastewater – polynuclear aromatic hydrocarbons Separatory funnel liquid-liquid extraction Polynuclear aromatic hydrocarbons
	US EPA 8270D	Semi-volatile organic compounds by gas chromatography/mass spectrometry (GC-MS)
	US EPA 8271	Assay of chemical agents in solid and aqueous samples by gas chromatograph/mass spectrometry, electron impact (GC/MS/EI)
nickel		······································
	APAT 3220B	NIA
	APHA 3113 DEV E22 DO-E22-1	Metals by electrothermal atomic absorption spectrometry NIA NIA
	EN ISO 11885	Water Quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP – OES)
	EN ISO 15586	Water Quality – Determination of trace elements using atomic absorption spectrometry with graphite furnace
	GI/PO/FQT/068	NIA
	ISO 8288 ISO 17294	Water Quality – Determination of cobalt, nickel, copper, zinc, cadmium and lead – Flame atomic absorption spectrometric methods Water Quality – Application of inductively coupled plasma mass
	LANGE KIT LCK 537	spectrometry (ICP-MS) – Part 2 – Determination of 62 elements NIA
	MEWAM 46	Nickel in potable waters 1981, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials,
	MEWAM 163 B	Environment Agency Inductively coupled plasma spectrometry 1996, Method B, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
	NEN 6966	NIA – Environment – Analysis of selected elements in water, eluates and destruaten – atomic emission spectrometry with inductively coupled plasma
	NFT 90-112	NIA Determination of a state of the state of
	US EPA 200.7	Determination of metals and trace elements in water and wastes by inductively coupled plasma-atomic emission spectrometry
	US EPA 200.8	Determination of trace elements in waters and wastes by inductively coupled plasma – mass spectrometry
	US EPA 3005A	Acid digestion of waters for total recoverable or dissolved metals for analysis by flame AA or ICP spectroscopy
	US EPA 6010C US EPA 6020	Inductively coupled plasma-atomic emission spectrometry Inductively coupled plasma-atomic emission spectrometry
	WAC/III/B W-METMSFL1	NIA NIA
nitrate		
	APAT 4020 APHA 4110B	NIA Ion chromatography with chemical suppression of eluent conductivity
	DIN 38406 EA/013-n	NIA NIA

nitrite

EN 26777	Water Quality – Determination of nitrite: molecular absorption
EN ISO 10304-1	spectrometric method Water Quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride,
EN ISO 10304-2	fluoride, nitrate, nitrite, phosphate and sulfate Water Quality. – Determination of dissolved anions by liquid chromatography of ions. Part 2 – Determination of bromide, chloride,
EN ISO 13395	nitrate, nitrite, orthophosphate and 81hysic81e in waste water Water Quality – Determination of nitrite nitrogen, nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection
ET044	NIA
ISO 7890-3	Water Quality – Determination of nitrate – Part 3: Spectrometric method using sulfosalicylic acid
LAND 65	NIA
LANGE LCK 339	NIA
NEN 6604	NIA – Water Quality – Determination of the concentration of ammonium, nitrate, nitrite, chloride, ortho-phosphate, sulphate and silicate with a discrete analysis and spectrophotometric detection
PN-82/C-04576/08	NIA – Determination of total nitrogen
US EPA 300.0	Determination of inorganic anions by ion chromatrography
US EPA 325.1 US EPA 325.2	Chloride (colorimetric, automated ferricyanide AAI) Chloride (colorimetric, automated ferricyanide AAII)
US EPA 9056A	Determination of inorganic anions by ion chromatography
W-NO3-SPC	NIA
APAT 4020	NIA
APAT 4050	NIA
APHA 4110B DIN 26777	Ion chromatography with chemical suppression of eluent conductivity NIA – Water Quality – Determination of nitrite: molecular absorption spectrometric method
DIN 38406 D9	NIA
EA/015a	NIA
EN ISO 10304-1	Water Quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate
EN ISO 10304-2	Water Quality. – Determination of dissolved anions by liquid chromatography of ions. Part 2 – Determination of bromide, chloride,
	nitrate, nitrite, orthophosphate and 81hysic81e in waste water
EN ISO 13395	Water Quality – Determination of nitrite nitrogen, nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric
LAND 39:2000	detection NIA
LANGE LCK 341	NIA
NEN 6604	NIA – Water Quality – Determination of the concentration of
	ammonium, nitrate, nitrite, chloride, ortho-phosphate, sulphate and silicate with a discrete analysis and spectrophotometric detection
US EPA 300.0	Determination of inorganic anions by ion chromatrography
US EPA 325.1	Chloride (colorimetric, automated ferricyanide AAI)
US EPA 325.2 US EPA 9056A	Chloride (colorimetric, automated ferricyanide AAII) Determination of inorganic anions by ion chromatography
WAC/III/C	NIA
W-NO2-SPC	NIA

## **OiW or TPHs**

APAT 5160	NIA
APHA 5520	Oil and grease
APHA 5520D	Oil and grease – Soxhlet extraction method
ASTM D 3921	Standard Test Method for Oil and Grease and Petroleum
ASTM D 3921	
	Hydrocarbons in Water
DEV H53	NIA
DIN 38409 H18	NIA – German Standard Methods for the Analysis of Water, Waste
	Water and Sludge; Summary Action and Material Characteristic
	Parameters (Group H); Determination of Hydrocarbons (H 18).
	Withdrawn 2000.
DIN 38409 H53	NIA – Hydrocarbon index by solvent extraction and GC
	(ISO 9377-4) (Withdrawn)
DS/R 209	NIA
EN ISO 9377-2	Water Quality – Determination of hydrocarbon oil index – Part 2:
EN 166 3317 2	
	Method using solvent extraction and gas chromatography
LAND 61:2003	NIA
LRG 002	NIA
MEWAM 77 A	The determination of hydrocarbon oils in waters by solvent extraction,
	infra-red absorption and gravimetry 1983,
	Method A, Standing Committee of Analysts, Methods for the
	Examination of Waters and Associated Materials,
	Environment Agency
MI029	NIA
MSZ 1484-12:2002	NIA – Water test Part 12 - Hexane extractable matter by gravimetry
NFM 07-203	NIA
NFT 90-203	NIA
SM 5520 C	Oil and grease – Partition-infrared method
SM-5520 F	Oil and grease – Hydrocarbons
SR 7877-2	NIA – Water Quality – Determination of petroleum products content.
	Spectrophotometric method
STN 830 540-4a	NIA
UNE EN 1484	NIA – Water analysis – Guidelines for the determination of total
UNE EN 1404	
	organic carbon (TOC) and dissolved organic carbon (DOC)
US EPA 418.1	Petroleum hydrocarbons, total recoverable. Withdrawn.
PAHs	
MSZ 1484-6:2003	NIA – Water test – Determination of polycyclic aromatic hydrocarbons
	by gas chromatography-mass spectrometry
ISO 15680	
130 13080	Water Quality – Gas-chromatographic determination of a number of
	monocyclic aromatic hydrocarbons, naphthalene and several
	chlorinated compounds using purge-and-trap and thermal desorption
ISO 17993	Water Quality – Determination of 15 polycyclic aromatic
	hydrocarbons (PAH) in water by HPLC with fluorescence detection
	after liquid-liquid extraction
ISO 28540	Water Quality – Determination of 16 polycyclic aromatic
130 20040	
	hydrocarbons (PAH) in water – Method using gas chromatography
	with mass spectrometric detection (GC-MS)
pentachlorbenzene	
CZ-SOP-D06-03-169	NIA – Based on CSN EN ISO 6468, US EPA 8081, DIN 38407-2, -
	Determination of organochlorine pesticides and other halogen
	compounds by gas chromatography method with electron capture
	detection
EN ISO 6468	Water Quality – Determination of certain organochlorine insecticides,
	polychlorinated biphenyls and chlorobenzenes – Gas
	chromatographic method after liquid-liquid extraction

	US EPA 542 US EPA 3510C US EPA 8270D W-OCPECD02	Determination of 86 Volatile Organic Compounds in Water by Gas Chromatography/Mass Spectrometry Separatory funnel liquid-liquid extraction Semi-volatile organic compounds by gas chromatography/mass spectrometry (GC-MS) NIA
рН	APAT 2060 APHA 4500 ASTM D 1293 BS 6068 2.50 DIN 38404 C5 DIN 38414 T2 DS 287 ISBN 0117514284 ISO 10523 <i>ISO 26149</i> MSZ 260-4 NEN 6411 NF T90-008 NS 4720	NIA NIA Standard test methods for pH of water Water Quality – Determination of pH NIA – Determination of pH value NIA NIA NIA Water Quality – Determination of pH <i>Water Quality – Determination of pH</i> NIA NIA – Water and sludge – Determination of acidity (pH) NIA NIA
	PN-90/C-04540.01 US EPA 150.1	NIA pH (Electrometric)
phenols	APAT 5070A1 APHA 5520C APHA 5530 ASTM D1783 DEV H16-3 DIN 38409 H16 DS 281 EN ISO 14402 ISO 6439 <i>ISO 8165-2</i> HACH 8047 HACH LANGE LCK 345	NIA Oil and grease – Partition-infared method Phenols NIA – Standard Test Methods for Phenolic Compounds in Water NIA NIA – German standard methods for the examination of water, waste water and sludge; general measures of effects and substances (group H); determination of the phenol index (H16) NIA Water Quality – Determination of phenol index by flow analysis (FIA and CFA) Water Quality – Determination of phenol index – 4-aminoantipyrine spectrometric methods after distillation <i>Water Quality – Determination of selected monovalent phenols – Part</i> <i>2: Method by derivatization and gas chromatography</i> NIA NIA
		Phenols in waters and effluents by gas chromatography, 4-aminoantipyrine and 3-methyl-2- benzo-thiazolinehydrazone 1981, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency The Determination of Microgram and Submicrogram amounts of Individual Phenols in River and Potable waters 1988, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials,
	MSZ 1484-1 NBN T91-501 NEN 6670 NFT 90-204	Environment Agency NIA – Water test Determination of phenol index NIA – Determination of the index phenol NIA – Photometric method for the determination of the content of volatile phenols NIA

nhosnha	TRAACS SS028128 US EPA 3510C US EPA 8270D WAC/IV/A/001 XP T90 109	NIA Separatory funnel liquid-liquid extraction Semi-volatile organic compounds by gas chromatography/mass spectrometry (GC-MS) NIA NIA
phospha	EN ISO 15681-1	Water Quality – Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) – Part 1: Method by flow injection analysis
	ISO 10304-1	Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate
	ISO 10304-2	Water Quality. – Determination of dissolved anions by liquid chromatography of ions. Part 2 – Determination of bromide, chloride, nitrate, nitrite, orthophosphate and 84hysic84e in waste water
selenium	SM 4110B	Ion Chromatography with chemical suppression of eluent conductivity
Selemun	APAT 3260A	NIA
	EN ISO 11885	Water Quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP – OES)
	ISO 9965	Water Quality – Determination of selenium – Atomic absorption spectrometric method (hydride technique)
	EN ISO 15586	Water Quality – Determination of trace elements using atomic absorption spectrometry with graphite furnace
	ISO 17294	Water Quality – Application of inductively coupled plasma mass spectrometry (ICP-MS) – Part 2: Determination of 62 elements
	ISO 17379-1	Water Quality – Determination of selenium – Part 1: Method using hydride generation atomic fluorescence spectrometry (HG-AFS)
	ISO 17379-2	Water Quality – Determination of selenium – Part 2: Method using hydride generation atomic absorption spectrometry (HG-AAS
-	MIP P-PRO-041	NIA NIA
г	PEFQ56 ag PC3 Ed No 3 US EPA 200.8	Determination of trace elements in waters and wastes by inductively coupled plasma – mass spectrometry
	US EPA 3005A	Acid digestion of waters for total recoverable or dissolved metals for analysis by flame AA or ICP spectroscopy
	US EPA 6010C US EPA 6020A	Inductively coupled plasma-atomic emission spectrometry Inductively coupled plasma-mass spectrometry
sulphate	WAC/III/B	NIA
oupliato	EN ISO 10304-1	Water Quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate
	EN ISO 10304-2	Water Quality. – Determination of dissolved anions by liquid chromatography of ions. Part 2 – Determination of bromide, chloride,
	ISO 9280	nitrate, nitrite, orthophosphate and 84hysic84e in waste water Water Quality – Determination of sulfate – Gravimetric method using barium chloride
ouch:-l-	SM 4110B	Ion Chromatography with chemical suppression of eluent conductivity
suphide	APAT 4160	NIA
	APHA 4110B APHA 4110B API 753	Ion chromatography with chemical suppression of eluent conductivity NIA
	ASTM D 4658	NIA – Standard Test Method for Sulfide Ion in Water

DEV D-27 DIN 38405 D26 HACH 8131 ISO 10530	NIA NIA NIA – Photometric determinatioon of dissolved sulphide by spectrometry NIA Water Quality – Determination of dissolved sulfide – Photometric method using methylene blue
MI091 MSZ 260-8	NIA NIA NIA Water Distances determination of the culoible
NEN 6608 SS 028117	NIA - Water - Photometric determination of the sulphide NIA
STN 65 6127	NIA - Fuel for engines. Determination of mercaptan and hydrogen sulphide by potentiometric titration
TOTAL 797 UOP 209	NIA NIA
UOP 683 US EPA 376.2 WAC/III/C	NIA Sulfide (colorimetric, methylene blue) NIA
suphide / mercaptan (sum)	
See sulphide above	
suphite	
APAT 4150B DIN 38405 D27	NIA NIA – Determination of readily liberated sulfide
HACH 8131	NIA
HACH HTP430	NIA
EN ISO 10304-3	Water Quality – Determination of dissolved anions by liquid chromatography of ions – Part 3: Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate
NEN 6604	NIA – Water Quality – Determination of the concentration of ammonium, nitrate, nitrite, chloride, ortho-phosphate, sulphate and silicate with a discrete analysis and spectrophotometric detection
SMWW 4500	NIA
STAS 7661-89	NIA
temperature APAT 2100	NIA
DIN 38404 C4	NIA - Standard Methods for Analysing of Water, Waste Water and Sludge; Physical and Physical-chemical parameters (Group C) Determination of Temperature (C4)
DIN 38404 C5	NIA – German standard methods for the examination of water, wastewater and sludge – Physical and 85hysic-chemical characteristics (group C) – Part 5: Determination of pH value (C 5)
US EPA 170.1	Temperature (Thermometric)
tetrachloroethylene	
EA-NLS EN ISO 10301	Water Quality – Determination of highly volatile halogenated hydrocarbons – Gas- chromatographic methods
EN ISO 15680	Water Quality – Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption
MEWAM 110	Determination of very low concentrations of hydrocarbons and halogenated hydrocarbons in Water 1984-5, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency

TOC	MEWAM 170 US EPA 524 US EPA 8010	The determination of volatile organic compounds in waters and complex matrices by purge and trap or by headspace techniques 1998, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry Halogenated volatile organics by gas chromatography
тос	APHA 5310B DIN 38409 H3 EN 1484	NIA NIA - TOC Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)
IS	BN 011752979 ISO 8245	NIA Water Quality - Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)
	MEWAM 157	The instrumental determination of total organic carbon and related determinands 1995, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment
	NEN 6633 US EPA 9060A WAC/III/D	Agency, ISBN 0117529796 NIA - Determination of chemical oxygen demand (COD) Total organic carbon NIA
toluene		
	APAT 5140 CGM/002-a DEV F-9-1 DIN 38407-F9	NIA NIA NIA NIA - German standard methods for water, wastewater and sludge; Together detectable substances (group F) Determination of benzene
		and some derivatives by gas chromatography (F9)
	EA-NLS EN ISO 10301	Water Quality - Determination of highly volatile halogenated hydrocarbons. Gas-chromatographic methods
E	N ISO 11423-1	Water Quality - Determination of benzene and some derivatives - Part 1: Head-space gas chromatographic method
	EN ISO 15680	Water Quality Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption
	ISO 10243-1	NIA
	ISO 11423-2	Water Quality - Determination of benzene and some derivatives - Part 2: Method using extraction and gas chromatography
	LPM 4189 <i>MEWAM 170</i>	NIA - Determination of volatile organic components; HS / GC The determination of volatile organic compounds in waters and
		complex matrices by purge and trap or by headspace techniques 1998, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
	US EPA 502	Volatile organic compounds in water by purge and trap capillary column gas chromatography with photoionization and electrolytic conductivity detectors in series
	US EPA 524	Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry
	US EPA 542	Determination of 86 Volatile Organic Compounds in Water by Gas Chromatography/Mass Spectrometry
	US EPA 602	Methods for organic chemical analysis of municipal and industrial wastewater - purgeable aromatics

US EPA 610	Methods for organic chemical analysis of municipal and industrial
US EPA 624	wastewater - polynuclear aromatic hydrocarbons Methods for organic chemical analysis of municipal and industrial
US EPA 5021A	wastewater - purgeables Volatile organic compounds in soils and other solid matrices using
US EPA 5030C US EPA 8010 US EPA 8015B US EPA 8020 US EPA 8021	equilibrium headspace analysis Purge-and-trap for aqueous samples Halogenated volatile organics by gas chromatography Non-halogenated organics using GC/FID Aromatic volatile organics by gas chromatography Aromatic and halogenated volatiles by gas chromatography using photoionization and/or electrolytic conductivity detectors
US EPA 8120 US EPQA 8260C	Chlorinated hydrocarbons by gas chromatography Volatile organic compounds by gas chromatography/mass
WAC/IV/A/016 W-VICGMS03	spectrometry (GC/MS) NIA - Headspace GC-MS NIA
total nitrogen APAT 4060	NIA
APHA 4500	NIA
DIN 38405 D9-2	NIA
DIN 38409 H12 EN 12260	NIA Water Quality - Determination of nitrogen - Determination of bound
21012200	nitrogen (TNb), following oxidation to nitrogen oxides
EN 25663	Water quality. Determination of Kjeldahl nitrogen. Method after
EN ISO 11732	mineralization with selenium Water Quality - Determination of ammonium nitrogen - Method by
EN 130 11732	flow analysis (CFA and FIA) and spectrometric detection
EN ISO 11905-1	Water Quality - Determination of nitrogen - Part 1: Method using oxidative digestion with peroxodisulfate
EN ISO 13395	Water Quality - Determination of nitrite nitrogen, nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection
ETG03	NIA
GI/PO/FQT/167	NIA Mater Quality Determination of Kieldahl sitragen. Method offer
ISO 5663	Water Quality - Determination of Kjeldahl nitrogen - Method after mineralization with selenium
ISO 6777	Water Quality - Determination of nitrite - Molecular absorption spectrometric method
LAND 59:2003	NIA
MI095:2008 MPI 067	NIA NIA
MSZ 260-12:1987	NIA
NEN 6481	NIA - Acceptance inspection of vertical external Broaching machines
NEN 6604	<ul> <li>Testing of the accuracy</li> <li>NIA - Water Quality - Determination of the concentration of ammonium, nitrate, nitrite, chloride, ortho-phosphate, sulphate and</li> </ul>
WAC/III/D	silicate with a discrete analysis and spectrophotometric detection NIA
total phosphorus APAT 4110	NIA
APHA 4550	NIA
DIN 38405 D11	NIA - Determination of total phosphorous after nitric/sulfuric acid
DO-E22-1	digestion NIA

	NIA
EN 1189	Water Quality. Determination of phosphorus. Ammonium molybdate
EN 100 0070	spectrometric method
EN ISO 6878	Water Quality Determination of phosphorus Ammonium
	molybdate spectrometric method
EN ISO 11885	Water Quality - Determination of selected elements by inductively
FTOOD	coupled plasma optical emission spectrometry (ICP - OES)
ETG02	NIA
GI/PO/FQT 019	NIA
HACH 8178	NIA
HACH 8190	NIA Matao O alita - Dataoni adia a faliana hada a kasia a hadia
ISO 10304-2	Water Quality - Determination of dissolved anions by liquid
	chromatography of ions - Part 2: Determination of bromide, chloride,
	nitrate, nitrite, orthophosphate and sulfate in waste water
ISO 15681-2	Water Quality - Determination of orthophosphate and total
	phosphorus contents by flow analysis (FIA and CFA) - Part 2: Method
	by continuous flow analysis (CFA)
LAND 58:2003	NIA
LANGE LCK 349	NIA
MI018:2006	NIA
MSZ 260-20	NIA
NEN 6966	NIA - Environment - Analysis of selected elements in water, eluates
	and destruaten - atomic emission spectrometry with inductively
	coupled plasma
US EPA 325.1	Chloride (colorimetric, automated ferricyanide AAI)
US EPA 365.3	Phosphorous, All Forms (Colorimetric)
WAC/III/B	NIA
total suspended solids APAT 2090B	NIA
APAT 2090B APH 2540D	Solids
BS 6621	NIA
CRM108	NIA
ČSN 757346/A	NIA
DEV H 9-2	NIA
DIN 38409 H2	NIA
EN 872	Water Quality. Determination of suspended solids. Method by
211072	filtration through glass fibre filters
ISO 11923	Water Quality - Determination of suspended solids by filtration
	through glass-fibre filters
LAND 46:2007	NIA
MSZ 260-3:1973	NIA
NBN 366	NIA
NEN 6484	NIA - Water Quality - Determination of Suspended Solids and the
	Residue on Ignition of Dry Mass - Method By Membrane Filtration
NEN 6621	NIA - Wastewater and sludge - Determination of the content of
	suspended solids and the glow of rest - Gravimetric method
NS 4733	NIA - Water analysis - Determination of suspended solids in waste
	water and their residue on ignition
SS ET042	NIA
STAS 6953:1981	NIA - Suspended matters
US EPA 160.2	Residue, Non-Filterable (Gravimetric, Dried at 103-105°C)
WAC/III/D/002	NIA
toxic metals	

See individual metals

#### trichloromethane

tricnioromethane		
	APAT 5150	NIA
	EA-NLS	
EN ISO 10301		Water Quality - Determination of highly volatile halogenated
		hydrocarbons. Gas-chromatographic methods
	EN ISO 15680	Water quality Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption
	MEWAM 110	Determination of very low concentrations of hydrocarbons and halogenated hydrocarbons in Water 1984-5, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
	MEWAM 170	The determination of volatile organic compounds in waters and complex matrices by purge and trap or by headspace techniques 1998, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
	US EPA 524	Measurement of purgeable organic compounds in water by capillary
	US EPA 624	column gas chromatography/mass spectrometry Methods for organic chemical analysis of municipal and industrial wastewater - purgeables
	US EPA 3510C	Separatory funnel liquid-liquid extraction
	US EPA 5030C	Purge-and-trap for aqueous samples
	US EPA 8010	Halogenated volatile organics by gas chromatography
	US EPA 8021	Aromatic and halogenated volatiles by gas chromatography using
	00 21 / 0021	photoionization and/or electrolytic conductivity detectors
	US EPA 8100	Polynuclear aromatic hydrocarbons
	US EPA 8270D	Semi-volatile organic compounds by gas chromatography/mass
	03 LFA 0210D	spectrometry (GC-MS)
venedium		spectrometry (GC-WS)
vanadium		NIIA
	APAT 3310	NIA
	DEV E-22	NIA
	DS 259	NIA - Water Quality - Determination of metals in water, soil, sludge and sediments - General principles and guidelines for determination
		by atomic absorption spectrophotometry in flame
	EN ISO 11885	Water Quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP - OES)
	EN ISO 15586	Water Quality - Determination of trace elements using atomic absorption spectrometry with graphite furnace
	ISO 17294	Water Quality - Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements
	SM 3111D	Metals by flame atomic absorption spectrometry
	US EPA 200.7	Determination of metals and trace elements in water and wastes by inductively coupled plasma-atomic emission spectrometry
	US EPA 200.8	Determination of trace elements in waters and wastes by inductively coupled plasma - mass spectrometry
	US EPA 6010C	Inductively coupled plasma-atomic emission spectrometry
	US EPA 6020A	Inductively coupled plasma-mass spectrometry
	WAC/III/B	NIA
	W-METMSFL2	NIA
vulanas		
xylenes		NIA
	APAT 5140	NIA
	CGM/002-a	NIA
	DEV F-9-1	NIA
	DIN 38407-F9	NIA

EA-NLS

EN ISO 10301	Water Quality - Determination of highly volatile halogenated hydrocarbons. Gas-chromatographic methods
EN ISO 15680	Water Quality - Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several
	chlorinated compounds using purge-and-trap and thermal desorption
ISO 10243-1	NIA
ISO 11423-2	Water Quality - Determination of benzene and some derivatives -
	Part 2: Method using extraction and gas chromatography
LPM 4189	NIA - Determination of volatile organic components; HS / GC
MEWAQM 170	The determination of volatile organic compounds in waters and complex matrices by purge and trap or by headspace techniques 1998, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
US EPA 502	Volatile organic compounds in water by purge and trap capillary column gas chromatography with photoionization and electrolytic conductivity detectors in series
US EPA 524	Measurement of purgeable organic compounds in water by capillary
	column gas chromatography/mass spectrometry
US EPA 542	Determination of 86 Volatile Organic Compounds in Water by Gas Chromatography/Mass Spectrometry
US EPA 602	Methods for organic chemical analysis of municipal and industrial
	wastewater - purgeable aromatics
US EPA 610	Methods for organic chemical analysis of municipal and industrial
	wastewater - polynuclear aromatic hydrocarbons
US EPA 624	Methods for organic chemical analysis of municipal and industrial
	wastewater - purgeables
US EPA 5021A	Volatile organic compounds in soils and other solid matrices using equilibrium headspace analysis
US EPA 5030C	Purge-and-trap for aqueous samples
US EPA 8010	Halogenated volatile organics by gas chromatography
US EPA 8015B	Non-halogenated organics using GC/FID
US EPA 8020	Aromatic volatile organics by gas chromatography
US EPA 8021	Aromatic and halogenated volatiles by gas chromatography using
	photoionization and/or electrolytic conductivity detectors Chlorinated hydrocarbons by gas chromatography
US EPA 8120 US EPA 8023	NIA
US EPQA 8260C	
	Volatile organic compounds by gas chromatography/mass spectrometry (GC/MS)
WAC/IV/A/016	NIA - Headspace GC-MS
W-VICGMS03	NIA
APAT 3113	NIA
APAT 3320	NIA
ASTM D 1976	NIA - Standard test method for elements in water by inductively- coupled argon plasma atomic emission spectroscopy
EN ISO 11885	Water Quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP - OES)
GI/PO/FQT/068	NIA
ISO 8288	Water Quality - Determination of cobalt, nickel, copper, zinc,
ISO 17294	cadmium and lead - Flame atomic absorption spectrometric methods Water Quality - Application of inductively coupled plasma mass
IT-A-018C	spectrometry (ICP-MS) - Part 2: Determination of 62 elements NIA
LAMGE KIT LCK 360	NIA

zinc

MEWAM 163 B	Inductively coupled plasma spectrometry 1996, Method B, Standing Committee of Analysts, Methods for the Examination of Waters and Associated Materials, Environment Agency
NEN 6966	NIA - Environment - Analysis of selected elements in water, eluates and destruaten - atomic emission spectrometry with inductively coupled plasma
NFT 90-112	NIA
SM 3120B	Inductively Coupled Plasma (ICP) method
US EPA 200.7	Determination of metals and trace elements in water and wastes by inductively coupled plasma-atomic emission spectrometry
US EPA 200.8	Determination of trace elements in waters and wastes by inductively coupled plasma - mass spectrometry
US EPA 3005A	Acid digestion of waters for total recoverable or dissolved metals for analysis by flame AA or ICP spectroscopy
US EPA 6010C	Inductively coupled plasma-atomic emission spectrometry
US EPA 6020	Inductively coupled plasma-mass spectrometry
WAC/III/B	NIA
W-METMSFL2	NIA

Note:NIA indicates no information available

# APPENDIX 2 STATISTICAL EQUATIONS

Bias (absolute), b	$\overline{\mathbf{x}} - \mathbf{x}_0$
Bias (percentage)	100 x̄ / x <sub>0</sub> R - 100
Bias (percentage fraction), b	100( x̄ - x <sub>0</sub> ) / x <sub>0</sub>
Limit of detection, LoD	f x $s_b$ where f is a factor usually between 3-5
Limit of quantification, LoQ	f x LoD where f is a factor usually between 2-4
Mean, $\bar{x}$ ,of a series of n replicated results	$(x_{1} + x_{2} + x_{3} + x_{4} +x_{n-2} + x_{n-1} + x_{n}) / n$ $\overline{x} = \frac{\sum_{i=1}^{n} x_{i}}{n}  \overline{x} = \frac{\sum_{i=1}^{i=n} x_{i}}{n}$
Minimum reporting value, MRV	See LoQ
Recovery (percentage), R	100 $\bar{x} / x_0$ 100 + b 100(C <sub>WS</sub> - C <sub>S</sub> ) / C <sub>ISA</sub>
Relative standard deviation, RSD	s/ x
When expressed as a percentage value, this is known as the coefficient of variation, CoV	s x 100 / x

Standard deviation, s	$\left(\begin{array}{c} \sum_{i=1}^{i=n} (\mathbf{x}_{i} - \mathbf{x})^{2} \\ \sum_{i=1}^{i=1} (\mathbf{x}_{i} - \mathbf{x})^{2} \\ \mathbf{x}_{i} = \sqrt{\frac{\sum_{i=1}^{i=n} (\mathbf{x}_{i} - \mathbf{x})^{2}}{n-1}} \\ s = \sqrt{\frac{\sum_{i=1}^{i=n} x_{i}^{2} - \frac{\left(\sum_{i=1}^{i=n} x_{i}\right)^{2}}{n-1}} \\ s = \sqrt{\frac{\sum_{i=1}^{i=n} x_{i}^{2} - \frac{\left(\sum_{i=1}^{i=n} x_{i}\right)^{2}}{n-1}}} $
Standard deviation (error) of the mean, SDM	s / n <sup>½</sup> 
Series of n replicated results	$X_1, X_2, X_3, X_4, \dots, X_{n-2}, X_{n-1}, X_n$
Uncertainty of measurement, UoM where t = two-sided t-value with n-1 degrees of freedom	$\overline{x} \pm t \frac{s}{\sqrt{n}}$ $(2 \times s) +  b $ $(3 \times s)$

See section 5 for explanation of terms and symbols.

# APPENDIX 3 SUMMARY COMMENTARIES OF METHOD ASSESSMENTS

This appendix will only be applicable at the time of publication. When new data are provided by operators and new assessments carried out, this table will become out of date, as new rankings are performed and methods are re-evaluated and re-prioritised. Listed below are summary details of the method assessments for 53 parameters. As already pointed out, see section 3, methods for parameters such as BTEX, PAHs, TPHs, phenols etc where groups of substances are included, are not assessed. For full details of the assessments see **Appendix 4**. Some methods appear to be ranked quite poorly mainly because there is little information available. If may be the case that if performance data were to be provided, these methods might become more highly rated. The little information that is available would suggest the methods possess the potential to be good methods in terms of their performance data that is available.

Where an AA-EQS value is given for a particular parameter and there is no information or data on the performance of a specific method, then an overall ranking value of 92 will be established. This would be based on ranking scores for precision, bias or recovery, LoD, costs and ease of use of 40, 40, 4, 4 and 4 respectively. This would represent a method of the lowest quality and be of the lowest priority. Where a method is reported to show very good precision and recovery, exhibits an acceptable LoD in terms of its associated critical level, and is cheap to operate and very easy to use, then ranking scores 10, 10, 1, 1 and 1 would be assigned and an overall ranking value of 23 will be established. This would represent a method of the highest quality and be of the highest priority. Depending on the quality of the method, an overall ranking value of between 23 and 92 will be expected. Thus, the actual overall ranking value itself is not an important factor, but the relative positions of the methods are important.

Where there is no AA-EQS value for a particular parameter and there is no information or data on the performance of a specific method, then an overall ranking value of 88 will be established. This would be based on ranking scores for precision, bias or recovery, indicative costs and ease of use of 40, 40, 4 and 4 respectively. This would represent a method of the lowest quality and be of the lowest priority. Where a method is reported to show very good precision and recovery, and is cheap to operate and very easy to use, then ranking scores 10, 10, 1 and 1 would be assigned and an overall ranking value of 22 will be established. This would represent a method of the highest quality and be of the highest priority. Depending on the quality of the method, an overall ranking value of between 22 and 88 will be expected. Thus, the actual overall ranking value itself is not an important factor, but the relative positions of the methods based on their ranking values are important.

PARAMETER Method	Overall ranking value	Comments
ALUMINIUM		
EN ISO 11885 EN ISO 15586 ISO 10566 MEWAM 116 C US EPA 200.7 US EPA 200.8 EN ISO 12020	25 25 35 45 45 45 65	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need not be assessed. Of the seven methods assessed, only two (EN ISO 11885 and EN ISO 12020) are mentioned in the CONCAWE survey. The other five methods have been added as methods that could have been used. Two methods, EN ISO 11885 and EN ISO 15586 are shown to be clearly better than the rest in terms of their overall ranking values (each with a ranking value of 25) based on their precision and recovery values. One method, ISO 10566, is rated slightly less (overall ranking value of 35) mainly due to a poorer recovery value. Three methods, MEWAM 116 C, US EPA 200.7 and US EPA 200.8 are ranked next (each with an overall ranking value of 45) due to poorer precision and recovery values. The method ranked lowest, EN ISO 12020 (overall ranking value of 65) shows poor precision and no information for recovery.
AMMONIA EN ISO 11905 US EPA 350.2 EN ISO 11732 (CFA)	24 32 54	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need not be assessed. Of the nine methods assessed, five are mentioned in the CONCAWE survey and four

EN ISO 11732 (FIA) EN ISO 14911	54 54	others, EN ISO 11905, ISO 5664, ISO 6778 and ISO 7150-2 have been added as methods that could have been used.
ISO 7150-2 ISO 7150-1 ISO 6778 ISO 5664	54 55 55 65	Two methods, EN ISO 11905 and US EPA 350.2 are shown to be clearly better than the rest in terms of their overall ranking values (ranking values of 24 and 32 respectively) based on their precision and recovery values. Most of the remaining methods are rated slightly less (overall ranking values between 54 and 55) mainly due to a lack of information
		being available for recovery values. The method ranked lowest, ISO 5664 (overall ranking value of 65) shows poor precision and no information for recovery.
AMMONIACAL NITROGEN		
US EPA 350.2	35	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
EN ISO 11732 (CFA)	54	not be assessed.
EN ISO 11732 (FIA)	54	Of the seven methods assessed, five are mentioned in the CONCAWE survey and two
ISO 7150-2	54	others, ISO 6778 and ISO 7150-2 have been added as methods that could have been
ISO 7150-1	55	used.
ISO 6778 ISO 5664	55 65	One method, US EPA 350.2 is shown to be clearly better than the rest in terms of its overall ranking value (ranking value of 35) based on its precision and recovery values. Most of the remaining methods are rated slightly less (overall ranking values between 54 and 55) mainly due to a lack of information being available for recovery values. The method ranked lowest, ISO 5664 (overall ranking value of 65) shows poor precision and no information for recovery.
EN ISO 17993 US EPA 8272 EN ISO 28540	36 40 49	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be assessed, and LoD estimations need to be taken into account to assess the LoQ compliance requirement <sup>(4)</sup> .
US EPA 8270 MEWAM 165 US EPA 610	49 56 68	Of the seven methods assessed, five are mentioned in the CONCAWE survey and two others (EN ISO 28540 and MEWAM 165) have been added as methods that could have been used.
US EPA 8100	69 69	Deen Used. Only two methods, MEWAM 165 and EN ISO 17993 satisfy both the regulatory UoM and LoQ compliance requirements <sup>(4)</sup> as defined in section 7.4.3.6, but see below. Two methods, EN ISO 17993 and US EPA 8272, are shown to be clearly better than the rest in terms of their overall ranking values (ranking values of 36 and 40 respectively) based on their precision and recovery values, even though method US EPA 8272 does not satisfy the LoQ requirement, mainly due to no information being available for LoD. Two other methods, EN ISO 28540 and US EPA 8270 were rated slightly less (each with overall ranking value of 49) due to a poorer precision and recovery values, although method US EPA 8270 does not satisfy the LoQ requirement mainly due to no information on the LoD Ses40 does not satisfy the LoQ requirement mainly due to no information on the LoD being available. The method ranked fifth, MEWAM 165 (overall ranking value of 56) due to poorer precision and very poor recovery values does however meet both the regulatory UoM and LoQ requirements. The two methods rated lowest, US EPA 610 and US EPA 8100 (overall ranking values of 68 and 69 respectively are due to very poor precision and recovery values, and neither method satisfies the UoM and LoQ requirements.
AOX	05	
EN ISO 9562	25	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need not be assessed.
		Only one standard method has been assessed as this is mainly due to a lack of information being available for other methods.
ARSENIC		
EN ISO 15586	25	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
ISO 17294	25	not be assessed.
ISO 11969	35	Of the eight methods assessed, three methods, ISO 11969, US EPA 200.7 and US EPA
US EPA 6010C	35	200.8, are not mentioned in the CONCAWE survey, but are added as methods could be
US EPA 200.7	35	used.
US EPA 200.8	45	Two methods, EN ISO 15586 and ISO 17294, are shown to be clearly better than the rest
EN ISO 11885	55	in terms of their overall ranking values (each with a ranking value of 25) based on their
US EPA 6020	75	precision and recovery values. Three methods, EN ISO 11969, US EPA 6010 and US EPA 200.7 are rated slightly less (each with overall ranking value of 35) mainly due to poorer recovery values, or in the case of US EPA 6010, poorer precision. Two methods, US EPA 200.8 and EN ISO 11885 are ranked next (overall ranking value of 45 and 55 respectively) due to poorer recovery values or no information being available. The method ranked lowest, US EPA 6020 (overall ranking value of 75) is due to very poor precision and no information for recovery.
BENZENE	~-	
EN ISO 15680	25	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be
US EPA 502.2	25	assessed, and LoD estimations need to be taken into account to assess the LoQ
US EPA 524.2	25	compliance requirement <sup>(4)</sup> .
US EPA 8260	25 35	Of the nine methods assessed and compared, eight are mentioned in the CONCAWE
US EPA 602	35 35	survey and one other (namely, MEWAM 170) has been added as a method that could have been used. One method, EN ISO 10201, not listed in the table but mentioned in the
US EPA 8020	35	have been used. One method, EN ISO 10301, not listed in the table but mentioned in the

MEWAM 170 US EPA 624 ISO 11423-1	35 37 46	survey did not show any performance data for this parameter. Five methods, EN ISO 15680, US EPA 502.2, US EPA 524.2, US EPA 8260 and MEWAM 170 satisfy both the regulatory UoM and LoQ compliance requirements <sup>(4)</sup> as defined in section 7.4.3.6. Of these five methods, four methods, EN ISO 15680, US EPA 502.2, US EPA 524.2 and US EPA 8260 are shown to be clearly better than the rest in terms of their overall ranking values (each with ranking values of 25) based on their precision and recovery values. One method, MEWAM 170 was rated slightly less (overall ranking value of 35) due to a poorer precision value. One method, US EPA 624, did not satisfy either of the UoM or LoQ compliance requirements <sup>(4)</sup> as defined, and was rated next poorest of all methods (overall ranking value of 37) due to a poor precision value and a high LoD value. ISO 11423-1 was rated the poorest method (overall ranking value of 46) due to poor precision and recovery values.
BENZO(b)FLUORANTHENE		
ISO 17993 MEWAM 165 ISO 7981-2 EN ISO 28540 US EPA 8270 US EPA 610 US EPA 8100	28 38 39 49 49 58 59	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be assessed, and LoD estimations need to be taken into account to assess the LoQ compliance requirement <sup>(4)</sup> . Of the seven methods assessed, five are mentioned in the CONCAWE survey and two others (EN ISO 28540 and MEWAM 165) have been added as methods that could have been used. None of the methods satisfies the regulatory LoQ compliance requirement <sup>(4)</sup> as defined in section 7.4.3.6, and only four methods, EN ISO 17993, MEWAM 165, ISO 7981 and EN ISO 28540, satisfy the regulatory UoM compliance requirement <sup>(4)</sup> as defined. One method, EN ISO 17993 is shown to be clearly better than the rest in terms of its overall ranking value (ranking value of 28) based on its precision and recovery values. Two methods, MEWAM 165 and ISO 7981-2, were rated slightly less (overall ranking values of 38 and 39 respectively) due to a poorer recovery value and precision value respectively. Two other methods, US EPA 8270 and EN ISO 28540 (each with ranking values of 49) were rated less due to poorer precision and recovery values respectively. Methods US EPA 610 and US EPA 8100 (overall ranking values of 58 and 59 respectively) were ranked lowest due to very poor precision and recovery values.
BENZO(k)FLUORANTHENE		
ISO 17993 MEWAM 165 ISO 7981-3 EN ISO 28540 US EPA 8270 US EPA 610 US EPA 8100	28 38 39 59 59 68 69	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be assessed, and LoD estimations need to be taken into account to assess the LoQ compliance requirement <sup>(4)</sup> . Of the seven methods assessed, five are mentioned in the CONCAWE survey and two others (EN ISO 28540 and MEWAM 165) have been added as methods that could have been used. None of the methods satisfies the regulatory LoQ compliance requirement <sup>(4)</sup> as defined in section 7.4.3.6, and only four methods, EN ISO 17993, MEWAM 165, ISO 7981-3 and EN ISO 28540, satisfy the regulatory UoM compliance requirement <sup>(4)</sup> as defined. One method, EN ISO 17993 is shown to be clearly better than the rest in terms of its overall ranking value (ranking value of 28) based on its precision and recovery values. Two methods, MEWAM 165 and ISO 7981-3, were rated slightly less (overall ranking values of 38 and 39 respectively) due to a poorer recovery value and precision value respectively. Two other methods, US EPA 8270 and EN ISO 28540 (each with ranking values of 59) were rated less due to poorer precision and recovery values respectively. Methods US EPA 610 and US EPA 8100 (overall ranking values of 68 and 69 respectively) were ranked lowest due to very poor precision and recovery values.
BENZO(ghi)PERYLENE ISO 17993 MEWAM 165 ISO 7981-2 EN ISO 28540 US EPA 8270 US EPA 610 US EPA 8100	28 28 38 49 49 68 69	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be assessed, and LoD estimations need to be taken into account to assess the LoQ compliance requirement <sup>(4)</sup> . Of the seven methods assessed, five are mentioned in the CONCAWE survey and two others (EN ISO 28540 and MEWAM 165) have been added as methods that could have been used. None of the methods satisfies the regulatory LoQ compliance requirement <sup>(4)</sup> as defined in section 7.4.3.6, and only three methods, EN ISO 17993, MEWAM 165, and EN ISO 28540, satisfy the regulatory UoM compliance requirement <sup>(4)</sup> as defined. Two methods, EN ISO 17993 and MEWAM 165 are shown to be clearly better than the rest in terms of their overall ranking values (each with ranking value of 28) based on their precision and recovery values. One method, ISO 7981-3, was rated slightly less (overall ranking value of 39) due to a poorer precision value. Two other methods, US EPA 8270 and EN ISO 28540 (overall ranking values of 49) were rated less due to poorer precision and recovery values respectively. Methods US EPA 610 and US EPA 8100 (overall ranking values of 68 and 69 respectively) were ranked lowest due to very poor precision and recovery values.

#### BENZO(a)PYRENE

BENZO(a)PTR	ENE		
	EN ISO 17993 MEWAM 165 ISO 7981-3 US EPA 8270 EN ISO 28540 US EPA 610 US EPA 8100	28 38 39 49 59 68 69	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be assessed, and LoD estimations need to be taken into account to assess the LoQ compliance requirement <sup>(4)</sup> . Of the seven methods assessed, five are mentioned in the CONCAWE survey and two others (EN ISO 28540 and MEWAM 165) have been added as methods that could have been used. None of the methods satisfies the regulatory LoQ compliance requirement <sup>(4)</sup> as defined in section 7.4.3.6, and four methods, EN ISO 17993, MEWAM 165, ISO 7981 and EN ISO 28540, satisfy the regulatory UoM compliance requirement <sup>(4)</sup> as defined. One method, EN ISO 17993 is shown to be clearly better than the rest in terms of its overall ranking value (ranking value of 28) based on its precision and recovery values. Two methods, MEWAM 165 and ISO 7981-3, were rated slightly less (overall ranking values of 38 and 39 respectively) due to a poorer recovery value and precision value respectively. Two other methods, US EPA 8270 and EN ISO 28540 (ranking values of 49 and 59 respectively, were rated less due to poorer recovery and precision values respectively) were ranked lowest due to very poor precision and recovery values.
BOD			were ranked lowest due to very poor precision and recovery values
BOD	EN 1899-2 MEWAM 130	65 65	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need not be assessed. Of the two methods assessed only one, EN 1899-2, is mentioned in the CONCAWE survey, the other, MEWAM 130, has been added as a method that could have been used. Both methods show similar performance data based on precision values. No performance data have been available from other methods cited in the survey.
CADMIUM			
	US EPA 200.8 EN ISO 15586 MEWAM 163B EN ISO 11885	27 28 37 38	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be assessed, and LoD estimations need to be taken into account to assess the LoQ compliance requirement <sup>(4)</sup> . Of the 10 methods assessed, eight are mentioned in the CONCAWE survey and two
	US EPA 6010C	38	others (US EPA 200.8 and MEWAM 163) have been added as methods that could have
	US EPA 200.7	38	been used.
	ISO 17294	39	None of the methods satisfies the regulatory LoQ compliance requirement <sup>(4)</sup> as defined in
	EN ISO 5961	39	section 7.4.3.6, but all methods satisfy the regulatory UoM compliance requirement <sup>(4)</sup> as
CHLORIDE	ISO 8288-1 US EPA 6020	59 69	defined. Two methods, US EPA 200.8 and EN ISO 15586, are shown to be slightly better than most of the methods in terms of their overall ranking values (ranking values of 27 and 28 respectively) based on their precision and recovery values. Six methods follow slightly behind (overall ranking values between 37 and 39) due to poorer precision and recovery values. Two methods, ISO 8288 and US EPA 6020, are ranked lowest (overall ranking values of 59 and 69 respectively) due to a lack of information being available for recovery values.
ONEONIDE	EN ISO 10304-2	24	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
	US EPA 300.1	24	not be assessed.
	ISO 9297	25	Of the six methods assessed, only one method, EN ISO 15682, is not mentioned in the
	EN ISO 15682	34	CONCAWE survey, and this method has been added as a method that could have been
	US EPA 9056	44	used.
	EN ISO 10304-1	54	Three methods, EN ISO 10304-2, US EPA 300.1 and ISO 9297, are shown to be slightly better than the rest in terms of their overall ranking values (ranking values of 24, 24 and 25 respectively) based on their precision and recovery values. Two methods, EN ISO 15682 and US EPA 9056, are rated slightly less (overall ranking values of 34 and 44 respectively) mainly due to poorer recovery values. One method, EN ISO 10304-1 is ranked lowest (overall ranking value of 54) due to a lack of information on the recovery value.
CHROMIUM			
	EN ISO 15586	25	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
	EN ISO 11885	35	not be assessed.
	EN 1233	35	Of the 10 methods assessed, two methods, US EPA 200.8 and MEWAM 163 are not
	ISO 9174	35	mentioned in the CONCAWE survey, but are added as methods that could have been
	ISO 17294	35 35	used. One method EN ISO 15586 is shown to be clightly better than the root in terms of its
	US EPA 6010C US EPA 200.7	35 45	One method, EN ISO 15586 is shown to be slightly better than the rest in terms of its overall ranking value (ranking value of 25) based on its precision and recovery values. Five
	MEWAM 163B	45 45	methods, EN ISO 11885, EN 1233, ISO 9174, ISO 17294 and US EPA 6010 are rated
	US EPA 200.8 US EPA 6020	45 65	slightly less (each with overall ranking value of 35) mainly due to poorer recovery values, or in the case of ISO 17294 and US EPA 6010, poorer precision. Three methods, US EPA 200.7, US EPA 200.8 and MEWAM 163 are ranked next lowest (each with overall ranking value of 45 respectively) due to poorer precision and recovery values respectively. The method rated lowest, US EPA 6020 is mainly due to a lack of information on the recovery value.

#### CHROMIUM (VI)

ormonito	EN ISO 23913 (FIA)	25	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
	EN ISO 23913 (CFA) EN ISO 11885 EN ISO 18412 ISO 11083 US EPA 200.8	25 35 35 35 45	not be assessed. Of the seven methods assessed, four methods, EN ISO 18412, EN ISO 23913 (FIA), EN ISO 23913 (CFA) and US EPA 200.7, are not mentioned in the CONCAWE survey, but are added as methods that could have been used. Two methods, EN ISO 23913 (FIA and CFA) are shown to be slightly better than the rest in
	US EPA 200.7	45	terms of their overall ranking values (each with a ranking value of 25) based on their precision and recovery values. Three methods, EN ISO 11885, EN ISO 18412 and ISO 11083 are rated slightly less (each with overall ranking value of 35) mainly due to poorer recovery values, or in the case of EN ISO 18412, poorer precision. Two methods, US EPA 200.7 and US EPA 200.8 are ranked lowest (each with overall ranking value of 45 respectively) due to poorer recovery values.
COBALT			respectively) due to poorer recovery values.
	ISO 17294	25	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
	MEWAM 163B	25	not be assessed.
	EN ISO 11885 EN ISO 15586	35 35	Of the seven methods assessed, three methods, MEWAM 163B, US EPA 200.7 and US EPA 200.8, are not mentioned in the CONCAWE survey, but are added as methods that
	US EPA 200.7	35	could have been used.
	US EPA 200.8 US EPA 6020A	35 65	Two methods, ISO17294 and MEWAM 163B are shown to be slightly better than the rest in terms of their overall ranking values (each with a ranking value of 25) based on their precision and recovery values. Four methods, EN ISO 11885, EN ISO 15586, US EPA 200.7 and US EPA 200.8 are rated slightly less (each with overall ranking value of 35) mainly due to poorer recovery values. One method, US EPA 6020 is ranked lowest (overall ranking value of 65) due to poorer precision value and no information on recovery.
COD		05	
	MEWAM 215 AB US EPA 410.4	25 35	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need not be assessed.
	MEWAM 215 CDE	54	Of the five methods assessed, two methods, MEWAM 215 AB and MEWAM 215 CDE are not mentioned in the CONCAWE survey, but are added as methods that could have been
	ISO 6060 ISO 15705	55 55	used.
			Two methods, MEWAM 215 AB and US EPA 410.4 are shown to be slightly better than the rest in terms of their overall ranking values (ranking values of 25 and 35 respectively) based on their precision and recovery values. Three methods, MEWAM 215 CDE, ISO 6060 and ISO 15705 are rated slightly less (overall ranking values of 54, 55 and 55 respectively) mainly due to recovery information not being available.
COPPER			respectively) mainly due to recovery information not being available.
	EN ISO 11885	25	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
	ISO 17294	25	not be assessed.
	US EPA 200.7	25 35	Of the nine methods assessed, two methods, MEWAM 163B and US EPA 200.8, are not mentioned in the CONCAWE survey, but are added as methods that could have been
	EN ISO 15586 US EPA 200.8	35	used.
	US EPA 6010	35	Three methods, EN ISO 11885, ISO 17294 and US EPA 200.7 are shown to be slightly
	MEWAM 163B	35	better than the rest in terms of their overall ranking values (each with a ranking value of 25)
	ISO 8288	55	based on their precision and recovery values. Four methods, EN ISO 15586, US EPA
	US EPA 6020A	65	200.8, US EPA 6010 and MEWAM 163 are rated slightly less (each with overall ranking value of 35) mainly due to poorer precision and recovery values. One method, ISO 8288 is ranked next lowest (overall ranking value of 55) due to no information on recovery being
			available. Method US EPA 6020 is rated lowest mainly due to a poor precision value and no information being available for recovery.
DICHLOR	OMETHANE		
	US EPA 524.2	25	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be
	US EPA 5030C	25	assessed, and LoD estimations need to be taken into account to assess the LoQ
	US EPA 8260	25	compliance requirement <sup>(4)</sup> .
	EN ISO 10301 (HS)	27	Of the 10 methods assessed, eight are mentioned in the CONCAWE survey and two
	US EPA 8020 US EPA 8010	32 38	others (US EPA 8260 and MEWAM 170) have been added as methods that could have been used.
	US EPA 624	53	Only three of the methods, US EPA 524.2, US EPA 5030 and US EPA 8260, satisfy the
	EN ISO 15680	55	regulatory LoQ and UoM compliance requirements <sup>(4)</sup> as defined in section 7.4.3.6.
	MEWAM 170A	55	These three methods are shown to be clearly better than the rest in terms of their overall
	EN ISO 10301(L-L)	57	ranking values (each with a ranking value of 25) based on their precision and recovery values. One method, EN ISO 10301 (HS) was rated slightly less (overall ranking value of 27) due to a much higher LoD value. Two other methods, US EPA 8020 and US EPA 8010 (overall ranking values of 32 and 38 respectively) were rated less due to poorer precision and recovery values. Methods US EPA 624, EN ISO 15680, MEWAM 170A and EN ISO 10301 (L-L) (overall ranking values of 53, 55, 55 and 57 respectively) were ranked poorest due to very poor precision and recovery values.

#### ETHYLBENZENE

EN ISO 15680	24	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
US EPA 542	24	not be assessed.
US EPA 502.2	24	Of the 12 methods assessed, two methods, EA-NLS and MEWAM 170, are not mentioned
US EPA 524.2	24	in the CONCAWE survey but have been added as methods that could have been used.
US EPA 5030C	24	Seven methods, EN ISO 15680, US EPA 542, US EPA 502.2, US EPA 524.2, US EPA
US EPA 8260	24	5030C, US EPA 8260 and EA-NLS, are shown to be slightly better than the rest in terms of
EA-NLS FFP	24	their overall ranking values (each with a ranking value of 23) based on their precision and
US EPA 624	31	recovery values. Four methods, US EPA 624, US EPA 8020, MEWAM 170 and US EPA
US EPA 8020	31	602 are rated slightly less (overall ranking values of 31, 31, 33 and 33 respectively) mainly
MEWAM 170	34	due to poorer precision values. ISO 11423-1 was rated the poorest method (overall ranking
US EPA 60	34	value of 54) due to poor precision and recovery values.
ISO 11423-1	54	
FLUORANTHENE		
ISO 17993	28	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be
EN ISO 28540	39	assessed, and LoD estimations need to be taken into account to assess the LoQ
ISO 7981-2	39	compliance requirement <sup>(4)</sup> .
MEWAM 165	48	Of the seven methods assessed, five are mentioned in the CONCAWE survey and two
US EPA 8270	49	others (EN ISO 28540 and MEWAM 165) have been added as methods that could have
US EPA 610	58	been used.
US EPA 8100	59	None of the methods satisfies the regulatory LoQ compliance requirement <sup>(4)</sup> as defined in section 7.4.3.6, and only four methods, EN ISO 17993, MEWAM 165, ISO 7981 and EN ISO 28540, satisfy the regulatory UoM compliance requirement <sup>(4)</sup> as defined. One method, EN ISO 17993 is shown to be clearly better than the rest in terms of its overall ranking value (ranking value of 28) based on its precision and recovery values. Two methods, ISO 7981-2 and EN ISO 28540, were rated slightly less (each with overall ranking values of 39) due to a poorer recovery value and poorer precision and recovery values of 48 and 49 respectively) were rated less due to poorer precision and poorer precision and poorer precision and recovery values of 58 and 59 respectively) were ranked lowest due to very poor precision and recovery values.
FLUORIDE		
EN ISO 10304-1	24	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
ISO 10359-1	34	not be assessed.
ISO 10359-2	34	Of the six methods assessed, one method, ISO 10359-2 is not mentioned in the
US EPA 300.1	34	CONCAWE survey, but has been added as a method that could have been used.
US EPA 340	34	One method, EN ISO 10304-1 is shown to be slightly better than the rest in terms of its
US EPA 9056	34	overall ranking value (ranking value of 24) based on its precision and recovery values. Two methods, ISO 10359-2 and US EPA 340 are rated slightly less (each with an overall ranking value of 34) mainly due to poorer precision values, whilst three other methods, ISO 10359-1, US EPA 300.1 and US EPA 9056 (rated the same) are due to poorer recovery values.
FREE CYANIDE		
EN ISO 14403	26	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
MEWAM 235 A2	26	not be assessed.
MEWAM 235 A3	36	Of the five methods assessed, three methods, MEWAM 235 A1, MEWAM 235 A2 and
MEWAM 235 A1 ISO 6703	46 66	MEWAM 235 A3 are not mentioned in the CONCAWE survey but have been added as methods that could have been used. Two methods, EN ISO 14403 and MEWAM 235 A2, are shown to be slightly better than the rest in terms of their overall ranking values (each with a ranking value of 26) based on their precision and recovery values. One method, MEWAM 235 A3 is rated slightly less
		(overall ranking value of 36) mainly due to poorer recovery value. The two remaining methods are rated lower due to poorer recovery (MEWAM 235 A1) or no information being available for recovery (ISO 6703). See also section 3.
INDENO(1,2,3-cd)PYRENE ISO 17993	28	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be
MEWAM 165	38	assessed, and LoD estimations need to be taken into account to assess the LoQ
ISO WD 7981-3	39	compliance requirement <sup>(4)</sup> .
EN ISO 28540	49	Of the seven methods assessed, five are mentioned in the CONCAWE survey and two
US EPA 610	58	others (EN ISO 28540 and MEWAM 165) have been added as methods that could have
US EPA 8100	59	been used.
US EPA 8270	69	None of the methods satisfies the regulatory LoQ compliance requirement <sup>(4)</sup> as defined in section 7.4.3.6, and only four methods, EN ISO 17993, MEWAM 165, ISO WD 7981-3 and EN ISO 28540, satisfy the regulatory UoM compliance requirement <sup>(4)</sup> as defined.

One method, EN ISO 17993 is shown to be clearly better than the rest in terms of its overall ranking value (ranking value of 28) based on its precision and recovery values. Two methods, MEWAM 165 and ISO WD 7981-3, were rated slightly less (overall ranking values of 38 and 39 respectively) due to a poorer recovery value and precision value

			respectively. One other method, EN ISO 28540 (ranking value of 49) was rated less due to poorer precision and recovery values. Methods US EPA 610 and US EPA 8100 (overall ranking values of 58 and 59 respectively) were ranked next due to very poor precision and recovery values. The lowest ranked method, US EPA 8270 (overall ranking value of 69) was due to very poor precision and recovery values
IRON			
	EN ISO 15586 EN ISO 11885 US EPA 6010 MEWAM 76 US EPA 200.7 US EPA 6020A	25 35 35 35 45 75	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need not be assessed. Of the six methods assessed only method MEWAM 76 is not mentioned in the CONCAWE survey, but has been added as a method that could have been used. One method, EN ISO 15586 is shown to be slightly better than the rest in terms of its overall ranking value (ranking value of 25) based on its precision and recovery values. Three methods, EN ISO 11885, US EPA 6010 and MEWAM 76 are rated slightly less (each with overall ranking value of 35) mainly due to poorer precision and recovery values. One method, US EPA 200.7 is ranked next lowest (overall ranking value of 45) due to poorer precision and recovery values, and method US EPA 6020 is rated lowest due to extremely poor precision and no information on recovery being available.
KJELDAHL NI	rogen		
	EN 25663 ISO 5663 MEWAM 126B	55 55 55	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need not be assessed. Of the three methods, two are mentioned in the CONCAWE survey and one (MEWAM 126B) is added as a method that could have been used. All methods are equally rated due to their precision values and lack of information on recovery values.
LEAD			· (1)
	US EPA 200.8 MEWAM 163 EN ISO 11885 EN ISO 15586 EN ISO 17294 US EPA 200.7	36 36 38 38 39 48	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be assessed, and LoD estimations need to be taken into account to assess the LoQ compliance requirement <sup>(4)</sup> . Of the nine methods assessed, seven are mentioned in the CONCAWE survey and two others (MEWAM 163 and ISO 17294) have been added as methods that could have been used.
MANGANESE	US EPA 6010 ISO 8288-1 US EPA 6020A	59 69 69	Only two of the methods, US EPA 200.8 and MEWAM 163, satisfy the regulatory LoQ and UoM compliance requirements <sup>(4)</sup> as defined in section 7.4.3.6. These two methods are rated slightly better than most of the methods in terms of their overall ranking values (each with a ranking value 36) based on their precision and recovery values. Three methods, EN ISO 11885, EN ISO 15586 and EN ISO 17294, are shown to be slightly worse in terms of their overall ranking values (ranking values of 38, 38 and 39 respectively) based on their precision and recovery values, but they do not satisfy the LoQ requirement as defined. One method follows slightly behind (overall ranking value of 48) due to its poorer precision and recovery values. One other method, US EPA 6010, is rated lower (overall ranking value of 59) due to poor precision. Two methods, ISO 8288 and US EPA 6020, are ranked lowest (each with an overall ranking value of 69) mainly due to a lack of information being available for recovery values.
MANGANEOE	EN ISO 11885	25	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
	EN ISO 17294 US EPA 200.8 MEWAM 163B EN ISO 15586 US EPA 200.7 MEWAM 76	25 25 25 35 45 45	not be assessed. Of the seven methods assessed, only method EN ISO 11885 is mentioned in the CONCAWE survey and the other six methods have been added as methods that could have been used. Four methods, EN ISO 11885, EN ISO 17294, US EPA 200.8 and MEWAM 163 are shown to be slightly better than the rest in terms of their overall ranking values (each with a ranking value of 25) based on their precision and recovery values. One method, EN ISO 15586, is rated slightly less (overall ranking value of 35) mainly due to poorer recovery value. Two methods are ranked lowest (each with an overall ranking value of 45) due to poorer precision and recovery values (US EPA 200.7) and very poor precision value
			(MEWAM 76).
MERCURY	EN 13506	25	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
	ISO 17852 ISO 17852 ISO 1483 EN ISO 12846 US EPA 200.7	25 25 35 35 35	not be assessed. Of the six methods assessed, four methods are mentioned in the CONCAWE survey and two methods, EN ISO 12846 and US EPA 200.7, have been added as methods that could have been used.
	EN ISO 12338	45	Two methods, EN 13506 and ISO 17862 are shown to be slightly better than the rest in terms of their overall ranking values (each with a ranking value of 25) based on their precision and recovery values. Three methods, ISO 1483, EN ISO 12846 and US EPA 200.7, are rated slightly less (each with an overall ranking value of 35) mainly due to poorer precision values for ISO 1483 and EN ISO 12846, and poorer recovery value for US EPA 200.7. The method rated lowest, EN ISO 12338 is due mainly to poorer precision and recovery values.

#### MTBE

NAPHTHA	EA NLS FFP MEWAM 170 US EPA 8260 EA NLS MCERTS US EPA 524.2	21 24 24 24 44	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need not be assessed. Of the five methods assessed, two methods are mentioned in the CONCAWE survey and three methods, EA NLS FFP, MEWAM 170 and EA NLS MCERTS, have been added as methods that could have been used. Four methods, EA NLS FFP, MEWAM 170, US EPA 8260 and EA NLS MCERTS, are shown to be slightly better than the remaining one in terms of their overall ranking values (ranking values of 21, 24, 24, and 24 respectively) based on their precision and recovery values. The method rated lowest, US EPA 524.2 is mainly due to poorer recovery.
	US EPA 524	25	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be
	ISO 17993 ISO 15680	26 27	assessed, and LoD estimations need to be taken into account to assess the LoQ compliance requirement <sup>(4)</sup> .
	MEWAM 165	46	Of the eight methods assessed, five are mentioned in the CONCAWE survey and three
	EN ISO 28540 US EPA 8270	49 49	others (US EPA 524.2, EN ISO 28540 and MEWAM 165) have been added as methods that could have been used.
NIGIZEI	US EPA 610 US EPA 8100	58 59	Only three methods, US EPA 524.2, EN ISO 17993 and MEWAM 165, satisfy both of the regulatory LoQ and UoM compliance requirements <sup>(4)</sup> as defined in section 7.4.3.6. Three methods, US EPA 524.2, EN ISO 17993 and ISO 15680, are shown to be clearly better than the rest in terms of their overall ranking values (ranking values of 25, 26 and 27 respectively) based on their precision and recovery values. Three methods, MEWAM 165, EN ISO 28540 and US EPA 8270, were rated less (overall ranking values of 46, 49 and 49 respectively) mainly due to poorer recovery values. Two other methods, US EPA 610 and US EPA 8100 (overall ranking values of 58 and 59 respectively) were ranked lowest due to very poor precision and recovery values.
NICKEL	US EPA 200.8	25	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be
	EN ISO 15586 ISO 17294 MEWAM 163	26 28 35	assessed, and LoD estimations need to be taken into account to assess the LoQ compliance requirement <sup>(4)</sup> . Of the 10 methods assessed, eight are mentioned in the CONCAWE survey and two others (MEWAM 46 and MEWAM 163) have been added as methods that could have
	US EPA 200.7 ISO 11885	37 38	been used.
	US EPA 6010C	47 57	Only three methods, US EPA 200.8, MEWAM 163 and US EPA 6020, satisfy both the regulatory UoM and LoQ compliance requirements <sup>(4)</sup> as defined in section 7.4.3.6.
NITRATE	MEWAM 46 ISO 8288 US EPA 6020A	57 58 65	regulatory UoM and LoQ compliance requirements <sup>17</sup> as defined in section 7.4.3.6. However, these three methods are clearly shown to be ranked quite differently with overall ranking values of 25, 35 and 65 respectively. Methods US EPA 200.8 and MEWAM 163 differ slightly in their recovery values, whilst for method US EPA 6020 there is no recovery information available. Four other methods, EN ISO 15586, ISO 17294, US EPA 200.7 and ISO 11885 (overall ranking values of 26, 28, 37 and 38 respectively) show ranking values similar to the two better methods, their LoD values do not satisfy the legislative requirement for LoQ, as they are either too high or information is not available. The ranking of other methods, US EPA 6010, MEWAM 46 and ISO 8288 (overall ranking values of 47, 57 and 58 respectively) either reflect their precision values or a general lack of information being available on recovery or LoD values. The ranking of method US EPA 6010 reflects poor precision and high LoD value; the ranking of method MEWAM 46 reflects good precision but high LoD value and no information on recovery, whilst the ranking of method ISO 8288 reflects good precision but no information for LoD and recovery values.
NIIKAIE	EN ISO 10304-1	24	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
	EN ISO 10304-2 US EPA 300 US EPA 9056 ISO 7890-3	24 24 34 54	not be assessed. Of the five methods assessed, all of which are mentioned in the CONCAWE survey methods EN ISO 10304-1, EN ISO 10304-2 and US EPA 300 are shown to be slightly better than the rest in terms of their overall ranking values (each with a ranking value of 24) based on their precision and recovery values. The method rated next lowest, US EPA 9056 is mainly due to poorer recovery. The method rated lowest, ISO 7890-3, is due to no
			information being available for the recovery.
NITRITE	EN ISO 10304-1	24	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
	EN ISO 10304-2	24	not be assessed.
	US EPA 9056 EN ISO 13395 (FIA)	24 34	Of the six methods assessed, one method, US EPA 300, is not mentioned in the CONCAWE survey and this method has been added as a method that could be used.
	US EPA 300	34 34	Three methods, EN ISO 10304-1, EN ISO 10304-2 and US EPA 9056 are shown to be
	EN ISO 13395 (CFA)	44	slightly better than the rest in terms of their overall ranking values (each with a ranking value of 24) based on their precision and recovery values. Two methods, EN ISO 13395 (FIA) and US EPA 300, are rated slightly lower mainly due to poorer precision and poorer recovery respectively. The method rated lowest, EN ISO 13395 (CFA), is due to poorer precision and recovery.

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PENTACHLOROBENZENE		
US EPA 542 EN ISO 6468	38 68	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be assessed, and LoD estimations need to be taken into account to assess the LoQ compliance requirement <sup>(4)</sup> . Of the two methods assessed, one is mentioned in the CONCAWE survey and the other, US EPA 542 has been added as a method that could have been used. None of the methods satisfy both the regulatory UoM and LoQ compliance requirements <sup>(4)</sup> as defined in section 7.4.3.6. The lower ranked method, EN ISO 6468, is mainly due to a lack of information on recovery.
PHOSPHATE EN ISO 10304-2 EN ISO 15681 EN ISO 10304-1 SM 4110B	24 24 44 44	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need not be assessed. Of the four methods assessed, only one is mentioned in the CONCAWE survey and three methods, EN ISO 15681, EN ISO 10304-1 and SM 4110B have been added as methods that could have been used. Two methods, EN ISO 10304-2 and EN ISO 15681 are shown to be slightly better than the rest in terms of their overall ranking values (each with a ranking value of 24) based on their precision and recovery values. Two methods, EN ISO 10304-1 and SM 4110B, are rated slightly worse (each with an overall ranking value of 44) due to poorer precision and recovery values.
SELENIUM EN ISO 11885	25	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
ISO 17379-1 ISO 17379-2 EN ISO 15586 ISO 9965 US EPA 6010 US EPA 200.8 US EPA 6020A	25 25 35 45 45 55 65	not be assessed. Of the eight methods assessed, four methods are mentioned in the CONCAWE survey and four methods, EN ISO 15586, ISO 9965, ISO 17379-1 and ISO 17379-2, have been added as methods that could have been used. Three methods, EN ISO 11885, ISO 17379-1 and ISO 17379-2 are shown to be slightly better than the rest in terms of their overall ranking values (each with a ranking value of 25) based on their precision and recovery values. One method, EN ISO 15586, is rated slightly less (overall ranking value of 35) mainly due to poorer precision. Two methods, ISO 9965 and US EPA 6010, are rated slightly worse (each with an overall ranking value of 45) due to poorer precision for US EPA 6010, and poor precision and recovery for ISO 9965. Method US EPA 200.8 is rated next lowest (overall ranking value of 55) due to poor recovery, and method US EPA 6020 is rated lowest (overall ranking value of 65) due to a lack of information being available for recovery and poor precision.
SULPHATE	04	
EN ISO 10304-1 EN ISO 10304-2 SM 4110B ISO 9280	24 24 44 54	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need not be assessed. Of the four methods assessed, none are mentioned in the CONCAWE survey and the methods, EN ISO 10304-1, EN ISO 10304-2, SM 4110B and ISO 9280 have been added as methods that could have been used. Two methods, EN ISO 10304-1 and EN ISO 10304-2 are shown to be slightly better than the rest in terms of their overall ranking values (each with a ranking value of 24) based on their precision and recovery values. One method, SM 4110B, is rated slightly less (overall ranking value of 44) mainly due to poorer precision and recovery. The method, ISO 9280, rated lowest is due to a lack of information being available for recovery.
SULPHIDE	24	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
ISO 10530 MEWAM 228B MEWAM 73A MEWAM 73A	34 44 54 54	not be assessed. Of the four methods assessed, only one method is mentioned in the CONCAWE survey and three methods, MEWAM 228B, MEWAM 73A and MEWAM 73B have been added as methods that could have been used. One method, ISO 10530 is shown to be slightly better than the rest in terms of its overall ranking value (ranking value of 34) based on its precision and recovery values. One method, MEWAM 228B, is rated slightly less (overall ranking value of 44) mainly due to poorer precision. The methods, MEWAM 73A and MEWAM 73B, are rated lowest due to a lack of information being available for recovery.
SULPHITE		
ISO 10304-3 SM 4500	54 64	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need not be assessed. Both methods assessed are mentioned in the CONCAWE survey. One method, ISO 10304-3 is shown to be slightly better than the other method in terms of its overall ranking value (ranking value of 54) based on its precision value. The other method, SM 4500 shows a poorer precision value, and also, no information on recovery.
	04	
EN ISO 15680 MEWAM 170 EN ISO 10301 (L-L)	24 24 25	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be assessed, and LoD estimations need to be taken into account to assess the LoQ compliance requirement <sup>(4)</sup> .

MEWAM 110 US EPA 524.2 US EPA 8010 EA-NLS FFP EN ISO 10301 (HS)	34 34 34 34 54	Of the eight methods assessed, none are mentioned in the CONCAWE survey and all have been added as methods that could have been used. Five methods, EN ISO 10301 (L-L), EN ISO 15680, MEWAM 170, US EPA 524.2 and EA-NLS FFP satisfy both the regulatory UoM and LoQ compliance requirements <sup>(4)</sup> as defined in section 7.4.3.6. Methods EN ISO 15680, MEWAM 170 and EN ISO 10301 (L-L) are shown to be slightly better than the rest in terms of their overall ranking values (overall ranking values of 24, 24 and 25 respectively) based on their precision and recovery values. Four methods, MEWAM 110, US EPA 524.2, US EPA 8010 and EA-NLS FFP (each with an overall ranking value of 34) differ slightly in their rated positions due to poorer precision values,
700		whilst method EN ISO 10301 (HS) shows poor precision and recovery values.
<b>TOC</b> EN 1484	35	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
MEWAM 157 (UV) MEWAM 157	54 65	not be assessed. Of the three methods assessed, only one method is mentioned in the CONCAWE survey and two methods, MEWAM 157 and MEWAM 157 (UV) have been added as methods that could have been used. The standard method, EN 1484 is shown to be slightly better than the rest in terms of its overall ranking value (ranking value of 35) based on its precision and recovery values. The other two methods differ in their ranking positions mainly due to a lack of information
		on recovery values.
TOLUENE		
EN ISO 15680	24	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
US EPA 542	24	not be assessed.
US EPA 502.2 US EPA 524.2 US EPA 5030C	24 24 24	Of the 12 methods assessed, 10 methods are mentioned in the CONCAWE survey and two methods, MEWAM 170 and EA-NLS, have been added as methods that could have been used.
US EPA 8260	24	Seven methods, EN ISO 15680, US EPA 542, US EPA 502.2, US EPA 524.2, US EPA
MEWAM 170	24	5030C, US EPA 8260 and MEWAM 170 are shown to be slightly better than the rest in
US EPA 624	31	terms of their overall ranking values (each with an overall ranking value of 24) based or
US EPA 8020	31	their precision and recovery values. Four methods, US EPA 624, US EPA 8020, US EPA
US EPA 602	34	602 and EA-NLS FFP are rated slightly less (overall ranking values of 31, 31, 34 and 34
EA-NLS FFP ISO 11423-1	34 44	respectively) mainly due to poorer precision, and for EA-NLS due to poorer recovery. ISC 11423-1 is ranked the poorest method (overall ranking value of 44) due to poor precision and recovery values.
TOTAL NITROGEN		and recovery values.
ISO 6777	21	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need not be assessed.
EN 12260	24	Of the nine methods assessed, all are mentioned in the CONCAWE survey.
EN 12260 EN ISO 13395 (FIA)	24 24	Five methods, ISO 6777, EN 12260, EN ISO 13395 (FIA), EN ISO 13395 (CFA) and EN ISO 11905-1 are shown to be slightly better than the rest in terms of their overall ranking
EN ISO 13395 (CFA)	24	values (ranking values of 21, 24, 24, 24 and 24 respectively) based on their precision and
EN ISO 11905-1	24	recovery values. Four methods, EN ISO 11732 (FIA), EN ISO 11732 (CFA), EN 25663 and
EN ISO 11732 (FIA)	54	ISO 5663 are rated slightly lower due to a lack of information on their recoveries.
EN ISO 11732 (CFA)	54	<i></i>
EN 25663	55	
ISO 5663	55	
TOTAL PHOSPHORUS	0.4	
ISO 10304-2	24	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
ISO 15681-2 EN ISO 11885	24 25	not be assessed. Of the four methods assessed, all are mentioned in the CONCAWE survey.
EN ISO 6878	55	Three methods, ISO 10304-2, ISO 15681-2 and EN ISO 11885 are shown to be slightly better than the remaining one in terms of their overall ranking values (ranking values of 24 24 and 25 respectively) based on their precision and recovery values. Method, EN ISC 6878 is ranked lowest due to a lack of information on the recovery.
TOTAL SUSPENDED SOLIDS		
EN ISO 872	54	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
ISO 11923	54	not be assessed.
EA-NLS FFP	54	Of the three methods assessed, two methods are mentioned in the CONCAWE survey and one method, EA-NLS, has been added as a method that could have been used. All methods are ranked equally due to their precision values and lack of information or recovery values.
TRICHLOROMETHANE		
US EPA 5030C	22	Since there is an AA-EQS value <sup>(8)</sup> the UoM compliance requirement <sup>(4)</sup> needs to be
EN ISO 15680 MEWAM 170A	24 24	assessed, and LoD estimations need to be taken into account to assess the LoQ compliance requirement <sup>(4)</sup> .
US EPA 524.2	24 24	Of the 10 methods assessed, seven are mentioned in the CONCAWE survey and three
EA-NLS	24	methods, MEWAM 170, MEWAM 110 and EA-NLS have been added as methods that
EN ISO 10301 (HS)	34	could have been used.

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US EPA 8010 US EPA 624 MEWAM 110	34 34 35	Five methods, EN ISO 10301 (L-L), EN ISO 15680, MEWAM 170, US EPA 524.2 and US EPA 5030 satisfy both the regulatory UoM and LoQ compliance requirements <sup>(4)</sup> as defined in section 7.4.3.6.
EN ISO 10301 (L-L)	58	Methods US EPA 5030C, EN ISO 15680, MEWAM 170A, US EPA 524.2 and EA-NLS are shown to be slightly better than the rest in terms of their overall ranking values (overall ranking values of 22, 24, 24, 24 and 24 respectively) based on their precision and recovery values. Four methods, EN ISO 10301 (HS), US EPA 8010, US EPA 624 and MEWAM 110 (overall ranking values of 34, 34, 34 and 35 respectively) differ slightly in their rated positions due to poorer precision values, and for EN ISO 10301 (HS) due to poor recovery. The lowest rated method, EN ISO 10301 (L-L) is due to no information being available for recovery or LoD.
VANADIUM		
EN ISO 15586	24	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
ISO 17294	24	not be assessed.
US EPA 6010C US EPA 200.7	24 34	Of the six methods assessed and compared, all are mentioned in the CONCAWE survey. Three methods, EN ISO 15586, ISO 17294 and US EPA 6010 are shown to be clearly
US EPA 200.8	44	better than the rest in terms of their overall ranking values (each with a ranking value of 24)
US EPA 6020A	74	based on their precision and recovery values. Two methods, US EPA 200.7 and US EPA 200.8 were rated slightly less (overall ranking value of 34 and 44 respectively) mainly due to poorer recovery values. The method ranked lowest, US EPA 6020 (overall ranking value of 74) shows very poor precision and no information available for recovery.
m-XYLENE		
US EPA 502.2	23	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
US EPA 524.2 US EPA 5030C	23 23	not be assessed. Of the five methods assessed and compared, all are mentioned in the CONCAWE survey.
US EPA 5050C US EPA 8260	23	Four methods, US EPA 502.2, US EPA 524.2, US EPA 5030 and US EPA 8260 are shown
US EPA 8021	51	to be clearly better than the rest in terms of their overall ranking values (each with a ranking value of 23) based on their precision and recovery values. The method ranked lowest, US EPA 8021 (overall ranking value of 51) shows no information available for precision.
o-XYLENE		
EN ISO 15680	24	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
ISO 11423-1	24	not be assessed.
US EPA 542 US EPA 502.2	24 24	Of the 10 methods assessed and compared, eight are mentioned in the CONCAWE survey and two methods, MEWAM 170 and EA-NLS FFP, have been added as methods that
US EPA 524.2	24	could have been used.
US EPA 5030C	24	All methods except US EPA 8021 are shown to be clearly better than the remaining one in
US EPA 8260	24	terms of their overall ranking values (each with a ranking value of 24) based on their
MEWAM 170	24	precision and recovery values. The method ranked lowest, US EPA 8021 (overall ranking
EA-NLS FFP	24	value of 51) shows no information available for precision.
US EPA 8021	51	
DEPA 502.2	23	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need
US EPA 524.2	23	not be assessed.
US EPA 5030C	23	Of the four methods assessed and compared, all are mentioned in the CONCAWE survey.
US EPA 8260	23	All methods are shown to be equally as good as each other in terms of their overall ranking values (each with a ranking value of 23) based on their precision and recovery values.
ZINC		
EN ISO 11885	25	Since there is no AA-EQS value both the LoQ and UoM compliance requirements <sup>(4)</sup> need not be assessed.
		Of the eight methods assessed, six methods are mentioned in the CONCAWE survey and two methods, EN ISO 15586, and MEWAM 163, have been added as methods that could have been used.
		nave been used. Three methods, EN ISO 11885, EN ISO 15586 and ISO 17294 are shown to be slightly better than the rest in terms of their overall ranking values (each with a ranking value of 25) based on their precision and recovery values. Three methods, US EPA 200.7, US EPA 200.8 and MEWAM 163 are rated slightly less (each with an overall ranking value of 35) mainly due to poorer recoveries. Method US EPA 6010 is rated next lowest (overall ranking value of 45) due to poor precision. Method US EPA 6020 is rated lowest (overall ranking value of 65) due to a lack of information being available for recovery and poor precision.

#### APPENDIX 4 METHOD ASSESSMENT TABLES

Where an AA-EQS value is given for a particular parameter and there is no information or data on the performance of a specific method, then an overall ranking value of 92 will be established. This would be based on ranking scores for precision, bias or recovery, LoD, costs and ease of use of 40, 40, 4, 4 and 4 respectively. This would represent a method of the lowest quality and be of the lowest priority. Where a method is reported to show very good precision and recovery, exhibits an acceptable LoD in terms of its associated critical level, and is cheap to operate and very easy to use, then ranking scores 10, 10, 1, 1 and 1 would be assigned and an overall ranking value of 23 will be established. This would represent a method of the highest quality and be of the highest priority. Depending on the quality of the method, an overall ranking value of between 23 and 92 will be expected. Thus, the actual overall ranking value itself is not an important factor, but the relative positions of the methods are important.

Where there is no AA-EQS value for a particular parameter and there is no information or data on the performance of a specific method, then an overall ranking value of 88 will be established. This would be based on ranking scores for precision, bias or recovery, indicative costs and ease of use of 40, 40, 4 and 4 respectively. This would represent a method of the lowest quality and be of the lowest priority. Where a method is reported to show very good precision and recovery, and is cheap to operate and very easy to use, then ranking scores 10, 10, 1 and 1 would be assigned and an overall ranking value of 22 will be established. This would represent a method of the highest quality and be of the highest priority. Depending on the quality of the method, an overall ranking value of between 22 and 88 will be expected. Thus, the actual overall ranking value itself is not an important factor, but the relative positions of the methods based on their ranking values are important.

Where an AA-EQS value is given for a particular parameter and there is no information or data on the performance of a specific method, then an overall ranking value of 92 will be established. This would be based on ranking scores for precision, bias or recovery, LoD, costs and ease of use of 40, 40, 4, 4 and 4 respectively. This would represent a method of the lowest quality and be of the lowest priority. Where a method is reported to show very good precision and recovery, exhibits an acceptable LoD in terms of its associated critical level, and is cheap to operate and very easy to use, then ranking scores 10, 10, 1, 1 and 1 would be assigned and an overall ranking value of 23 will be established. This would represent a method of the highest quality and be of the highest priority. Depending on the quality of the method, an overall ranking value of between 23 and 92 will be expected. Thus, the actual overall ranking value itself is not an important factor, but the relative positions of the methods are important.

Where there is no AA-EQS value for a particular parameter and there is no information or data on the performance of a specific method, then an overall ranking value of 88 will be established. This would be based on ranking scores for precision, bias or recovery, indicative costs and ease of use of 40, 40, 4 and 4 respectively. This would represent a method of the lowest quality and be of the lowest priority. Where a method is reported to show very good precision and recovery, and is cheap to operate and very easy to use, then ranking scores 10, 10, 1 and 1 would be assigned and an overall ranking value of 22 will be established. This would represent a method of the highest quality and be of the highest priority. Depending on the quality of the method, an overall ranking value of between 22 and 88 will be expected. Thus, the actual overall ranking value itself is not an important factor, but the relative positions of the methods based on their ranking values are important.

Non-organic

input, as appropriate into the yellow-shaded area, the name of parameter.

ALUMINIUM

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of yg/1. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank.

Method	Matrix	Precision	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
reference		8		8	% µg/i	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of CLoI			ORDER
EN ISO 11885	WM	2.6		97.1	100	2	2	CCC CCC	00	25
EN ISO 13386	WM	3.9		101.5	1	2	2	CCC CCC	00	25
ISO 10566	S	1.9		91.7	2	2	2	CCC CCC	00	35
EN ISO 12020	WM	8.1				2	2	566	00	99
MEWAM 116 C	RW	5.4		105.5	0.02	2	N	566	00	45
US EPA 200.7	ш	7.8		68	20	2	N	566	00	45
US EPA 200.8	ш	5.4		94.6	1.7	2	N	566	00	45
						If 0, does not comply	If 0, does not comply			
						If 1, complies	If 1, complies			
						If 2, no LoQ requirement	If 2, no UoM requirement			

DW drinking water GW ground water RW river water ReW reagent water

new reagent water AS aqueous solution AdW acid-digested water

WW waste water

lE industrial effluent SE sewage effluent

SE sewage effluent SS synthetic standard

U unknown

## Non-organic

Input, as appropriate into the yellow-shaded area, the name of parameter

AMMONIA

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yelliow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank	ethod as ap	propriate into the y	vellow-shaded	area, if no data a	vailable leave blank					
Method reference	Matrix	Precision	Bibs	Recovery	Recovery Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
		R	R	R	Hg/I	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of Cloi	50 % of CLoI			ORDER
EN ISO 11732 (CFA)	ш	1.2				2	2	eec	000	75
EN ISO 11732 (FIA)	ш	2.1				2	2	eee	000	7
EN ISO 11905	ш	1.2		86	20	2	2	tee tee	000	24
EN ISO 14911	35	4.1				2	2	eec	000	7
150 7150-1	SE	1.9			60	2	2	eec G	00	8
150 7150-2	SE	1.4			30	2	2	CCC CCC	000	75
150 3664	SE	8.9			200	2	2	55	00	99
150 6778	SE	3.1				2	2	55	00	5
US EPA 330.2	ReW	6.4		103		2	2	566	00	32
						If 0, does not comply	If 0, does not comply			
						If 1, complies	If 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

DW drinking water GW ground water RW river water ReW reagent water AS aqueous solution AdW acid-digested water AdW acid-digested water AdW acid-digested water GE industrial effluent SE synthetic standard U unknown

input, as appropriate into the yellow-shaded area, the name of parameter AMMONIACAL NITROGEN Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-chaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank	ethod as app	propriate into the y	ellow-shaded a	rea, if no data av	vailable leave blank					
Method reference	Matrix	Precision	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
		R	æ	R	Hg/I	LoQ. Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of CLoI			ORDER
EN ISO 11732 (CFA)	ш	12				2	2	eec	000	25
EN ISO 11732 (FIA)	ш	2.1				2	2	eec	000	2
150 7150-1	35	6.1			60	2	2	eec	00	55
150 7150-2	35	14			30	2	2	eec	000	54
150 3664	SE	6.8			200	2	2	eec	00	65
150 6778	SE	3.1				2	2	eec	00	55
US EPA 330.2	ReW	6.4		103		2	2	88	00	35
						If 0, does not comply	If 0, does not comply			
						If 1, complies	If 1, complies			
						If 2 , no LoQ requirement	If 2, no UoM requirement			

ReW reagent water DW drinking water GW ground water RW river water

AS aqueous solution

AdW acid-digested water WW waste water

IE industrial effluent

SE sewage effluent

SS synthetic standard U unknown

Organic

Input, as appropriate into the yellow-shaded area, the name of parameter

## ANTHRACENE

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank. 0.1

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

#### AA-EQS

input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

Method reference	Matrix	Precision	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
		æ	æ	æ	Hg/I	LoQ Requirement 30 % of CLOI	UoM Requirement 50 % of CLOI			RANKING ORDER
EN ISO 28540 :2011	RW	6.6		63.5		0	1	eec	00	49
	ш	23.8		61.7	0.66	0	•	eec	00	89
	5	23.8		61.7		•	•	eec	00	69
US EPA 8270 C &D	GW	21.1		80.7		•	•	eec	00	49
	GW	11		101		0	1	eec	0	40
	GW	11		8	0.004	1	1	eec	00	56
IS ISO 17993:2002	DW	7		<b>5</b> .68	0.01	1	1	eec	00	36
						If 0, does not comply If 1, complies	If 0, does not comply If 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

DW drinking water GW ground water RW river water REW reagent water AS aqueous solution AdW acid-digested water WW waste water IE industrial effluent SS synthetic standard

U unknown

input, as appropriate into the yellow-shaded area, the type of analysis as Grganic or Non-organic	e into the ye	Now-shaded area,	the type of ana	Nsis as Organic o	r Nan-organic					
Non-organic										
input, as appropriate into the yellow-shaded area, the name of parameter	e into the ye	Bow-shaded area,	, the name of pa	rameter						
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Input, as appropriate	e into the ye	clow-shaded area.	, the critical leve	I of interest (CLo	() in units of µg/L This o	ould pe an EQS value, a permit co	input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of ug/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank	level, etc. If none, le	cave blank.	
input, as appropriate	e into the ye	Now-shaded area,	whether this is	an EQS value, pe	rmit concentration, pro	input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.	ie, leave plant.			
input data for each method as appropriate into the vellow-shaded area, if no data available leave blank	nethod as a	opropriate into th	e vellow-shaded	area, if no data	svallable leave blank					
Method reference	Metrix	Precision	- E	Recovery	Limit or detection mg/l	LoQ = 3 x LoD LoQ Requirement 30 % of CLot	UoM Equirement 50 % of CLOI	Indicative cost	Ease of Use	OVERALL RANKING ORDER
EN ISO 9362	3	16.9		96.3		2	2	ecc.	90	25
						If 0, does not comply If 1, complies If 2, no LoQ requirement	If 0, does not comply If 1, complies If 2, no UoM requirement			
DW drinking water										
GW ground water										
RW river water										
ReW reagent water	5									
AS aqueous solution	5									
AdW acid-digested water	d water									
WW waste water										
IE industrial effluent	t									
SE sewage effluent	4									
SS synthetic standard	pue									
U unknown										

Non-organic

Input, as appropriate into the yellow-shaded area, the name of parameter

Input, as appropriate into the yellow-shaded area, the critical level of interest (GLoI) in units of yg/I. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank. ARSENIC

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

Method	Matrix	Precision	Bias	Recovery	Recovery Limit of detection	LoQ=3xLoD	UoM=3xs	Indicative cost Ease of Use	Ease of Use	OVERALL
reference		*	*	*	j₀a	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of CLoI			ORDER
EN ISO 11885	MM	m			100	2	2	ж,	00	22
EN ISO 15586	MM	4		8	1	2	2	eee	00	22
ISO 17294	ង	3.4		97.1		2	2	eee	00	22
ISO 11969	M	3.9		106		2	2	eee	00	35
US EPA 6010C	ADW	15.8		96.3	35	2	2	eee	00	35
US EPA 6020	SA	27.6				2	2	eee	00	75
US EPA 200.7	ш	1.7		8	69	2	2	eee	00	35
US EPA 200.8	ш	6.0		75.1	0.4	2	2	ЭЭЭ	00	45
						If 0, does not comply	If 0, does not comply			
						If 1, complies	If 1, complies			

If 2, no UoM requirement

lf 2, no LoQ requirement

DW drinking water GW ground water RW river water ReW reagent water AS aqueous solution AdW acid-digested water WW waste water IE industrial effluent SE sewage effluent SS synthetic standard U unknown

Input, as appropriate into the yellow-shaded area, the name of parameter

BENZENE

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank. 9

Input, as appropriate into the yelliow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

AA-EOS

Limit of detection Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank Recovery Bie: Precision Matrix Method reference

Method reference	Metrix	Precision %	Sies N	Recovery	Limit of detection µg/l	LoQ = 3 x LoD LoQ Requirement 30 % of CLoI	UoM = 3 x s UoM Requirement 50 % of CLol	Indicative cost Ease of Use	Ease of Use	OVERALL RANKING ORDER
EN ISO 13680	GW	3.9		104	0.1	1	1	8	000	54
US EPA 302.2	ReW	1.6		57	0.01	1	1	8	000	24
US EPA 524.2	ReW	5.7		97	0.04	1	1	8	000	24
US EPA 602	Þ	20		92.6	0.2	1	•	8	000	뷺
US EPA 8260	AS	5.7		97	0.04	1	1	8	000	24
US EPA 624	Þ	22.4		66	4.4	•	•	8	000	36
US EPA 8020	AS	20		92.6	0.2	1	•	8	000	34
MEWAM 170	Μ	11.7		104	0.14	1	1	8	000	쳤
						If 0, does not comply	If 0, does not comply			
						If 1, complies	If 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

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Input, as appropriate into the yellow-shaded area, the name of parameter Organic

# BENZO(a)PYRENE

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank. 0.00017

Input, as appropriate into the yelliow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

## AA-EQS

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

Method reference	Matrix	E.	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
		R	æ	R	I/SH	LoQ Requirement 30 % of CLoI	UoM Requirement 50 % of CLoI			RANKING
EN ISO 28340 :2011	WM	10.1		61.4		•	1	eee	00	59
US EPA 610	ш	29.7		36	0.023	•	•	eee	00	89
US EPA 8100	5	29.7		36		•	•	eee	00	69
US EPA 8270 C &D	GW	30.1		06		•	•	eee	00	49
SO 7981-2	22	15.2		91.2		0	1	eee	00	39
EN ISO 17993	SS	2.8		93.7	0.01	•	1	eee E	00	28
MEWAM 165	GW	3.6		79	0.001	•	1	eee	00	38
						If 0, does not comply	If 0, does not comply			

If 2, no UoM requirement If 1, complies

If 2, no LoQ requirement If 1, complies

Input, as appropriate into the yellow-shaded area, the name of parameter Organic

BENZO(b)FLUORANTHENE

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank. 0.00017

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank AA-EQS

Limit of detection Recovery BilBS Precision Matrix Method reference

Method reference	Matrix	Precision B	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost Ease of Use	Ease of Use	OVERALL
		8	*	*	hg/I	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of CLoI			ORDER
EN ISO 28540 :2011	WM	10.3		84.4		•	1	eee	00	49
US EPA 610	ш	29.6		78	0.018	•	•	566	00	58
US EPA 8100	5	29.6		78		•	0	55	00	59
US EPA 8270 C &D	GW	27.4		91.2		•	0	ecc	00	49
ISO 7981-2	SS	13.7		90.4		•	1	666	00	39
ISO 17993	DW	2.4		97.6	0.01	•	1	666	00	28
<b>MEWAM 165</b>	GW	33		8	0.001	•	1	666	00	38
						If 0, does not comply If 1, complies	If 0, does not comply If 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

AdW acid-digested water SS synthetic standard AS aqueous solution IE industrial effluent ReW reagent water SE sewage effluent DW drinking water GW ground water WW waste water **RW river water** 

U unknown

#### Organic

Input, as appropriate into the yellow-shaded area, the name of parameter

# BENZO(ghi)PERVLENE

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank. 0.00017

# Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

# AA-EQS

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

2 = 3 × LoD UoM = 3 × 5 tequirement UoM Requirement	LoQ = 3 x LoD LoQ Requirement	LoQ = 3 x LoD LoQ Requirement	Recovery Lumit of detection LoQ = 3 × LoD % µg/i LoQ, Requirement	Bitss Recovery Limit of detection LoQ = 3 × LoD % % μg/l LoQ Requirement	ion Bass Recovery Limit of detection LoQ = 3 × LoD % % µg/i LoQ Requirement
% of C					
•	•	63.3 0	63.3 0	10 63.3 0	WW 10 63.3 0
•	0.076 0	44.3 0.076 0			44.3
•	•	44.3 0	44.3 0	25.8 44.3 0	
•	•	97.1 0	97.1 0	49.1 97.1 0	GW 49.1 97.1 0
•	•	93.1 0	93.1 0	17.9 53.1 0	
•	0.01 0	93 0.01 0			
•	0.001	93 0.001 0			55
es not (	If 0, does not comply	If 0, does not (	If 0, does not (	If 0, does not	If 0, does not
comp	If 1, complies	lf 1, comp	lf 1, comp	If 1, comp	lf 1, comp
Q req	If 2, no LoQ req	If 2, no LoQ req	If 2, no LoQ req	If 2, no LoQ requirement	If 2, no LoQ req

DW drinking water

GW ground water RW river water

AS aqueous solution ReW reagent water

AdW acid-digested water

WW waste water

IE industrial effluent SE sewage effluent

SS synthetic standard U unknown

Organic

Input, as appropriate into the yellow-shaded area, the name of parameter BENZO(k)FLUORANTHENE

Input, as appropriate into the yelliow-shaded area, the critical level of interest [CLoI] in units or µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank. 0.000

Input, as appropriate into the yelliow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

AA-EQS

input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

Method reference Matrix	Matrix	Precision E	Bias	Recovery	ery Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost Ease of Use	Ease of Use	OVERALL
		R	8	R	l∕8H	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of CLoi			ORDER
EN ISO 28540 :2011	WW	13.3		58.5		•	1	555	00	29
US EPA 610	ш	40.7		96	0.017	•	•	555	00	89
US EPA 8100	5	40.8		38		•	•	555	00	69
US EPA 8270 C &D	GW	30.3		83.4		•	•	566	00	59
ISO 7981-2	SS	13.7		93.1		•	1	555	00	39
ISO 17993	SS	2		95.7	0.01	•	1	666	00	28
<b>MEWAM 165</b>	GW	23		8	0.001	•	1	666	00	38
						If 0, does not comply	If 0, does not comply			
						If 1, complies	If 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

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Non-organic Input, as appropriate into the yellow-shaded area, the name of paremeter

input, as appropriate into the yellow-shaded area, the name of paramete BOD

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave plank.

Input date for each I	method as a	ppropriate into the	e yellow-shaded	tiares, if no data t	input data for each method as appropriate into the yellow-shaded area, if no data available leave blank					
Method reference Matrix	Matrix	Precision %		Recovery	Recovery Limit of detection % mg/	LoQ = 3 x LoD LoQ Requirement 30 % of CLot	UoM = 3 x s UoM Requirement 30 % of CLOI	Indicative cost	Ease of Use	OVERALL RANKING ORDER
EN 1899-2	GW.	7.6				2	2	eec.	0.0	65
MEWAM 130	55	7.4				2	2	SEE	0.0	65
						If 0, does not comply If 1, complies	If 0, does not comply If 1, complies			
DW drinking water GW ground water										
RW river water ReW reagent water AS aqueous solution	5 5									

AdW acid-digested water

IE industrial effluent SE sewage effluent

WW waste water

55 synthetic standard U unknown

Non-organic

118

Input, as appropriate into the yellow-shaded area, the name of parameter

CADMIUM

input, as appropriate into the yellow-shaded area, the critical level of interest (CLof) in units of Hg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

0.23

input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as AA-EOS

Input data for each	method as a	ppropriate into th	te yellow-shade	d area, if no data	input data for each method as appropriate into the yellow-shaded area, if no data available leave blank					
Method	Matrix	Precision	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
reference		æ	R	R	I/Bri	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of CLoI			ORDER
EN ISO 11885	WM	2.9		93.8	100	•	1	eee	00	38
EN ISO 13386	WW	3.1		102.5	0.1	•	1	ecc	00	28
ISO 17294	8	6.8		99.1		•	1	666	00	39
EN ISO 3961	5	6.8		104.2		•	1	999	00	39
150 8288-1	REW	2.4				•	1	eee	00	<mark>8</mark> 9
US EPA 6010C	ADW	14.7		101.7	2.3	•	1	ecc	00	38
US EPA 6020	AS	5.9				•	1	eee	00	69
US EPA 200.7	ш	3.1		84	1	•	1	666	00	38
US EPA 200.8	ш	2.8		102	0.03	•	1	ecc	00	72
MEWAM 1638	×	1.2		92.6	0.04	•	1	555	00	37
						If 0, does not comply	If 0, does not comply			

If 2, no UoM requirement

If 2, no LoQ requirement

If 1, complies

If 1, complies

Non-organic

Input, as appropriate into the yellow-shaded area, the name of parameter

### CHLORIDE

input, as appropriate into the yellow-shaded area, the critical level of interest [CLo1] in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

Indicative cost Ease of Use			EEE 000	<b>ECE</b> 000 000	<b>CCC</b> 000 <b>CCC</b> 000 <b>CCC</b>	600 600 600 600 600 600 600 600	CCC 000 CCC 000 CCC 000 CCC 000 CCC	
00M = 3 X S	UoM Requirement 50 % of CLoI		2	7 7	~ ~ ~	~ ~ ~ ~	~ ~ ~ ~ ~	~ ~ ~ ~ ~
	LoQ. Requirement 30 % of CLoI	,	7	V 14	N N V	N N N V	N N N N	N N N N N
Recovery Limit of detection	NgH %			101	101 94.3	101 94.3 100	101 94.3 100 88.7	101 94.3 100 82.7
	R			9	9 7	40 M 10	40 ct ct	4 Cl -0 Cl -0
Matrix Precision	8	IE 2.2		IE 1.96	IE 1.96 WW 1.12			
Method reference		EN ISO 10304-1		EN ISO 10304-2	EN ISO 10304-2 EN ISO 15682	EN ISO 10304-2 EN ISO 13682 ISO 9297	EN ISO 10304-2 EN ISO 15682 ISO 9297 US EPA 300.1	EN ISO 10304-2 EN ISO 13682 ISO 9297 US EPA 300.1 US EPA 9036

If 2, no UoM requirement

If 2, no LoQ requirement

DW drinking water GW ground water RW river water REW reagent water AS aqueous solution AdW acid-digested water WW waste water IE industrial effluent SE synthetic standard U unknown

input, as appropriate into the yellow-shaded area, the name of parameter

CHROMIUM (VI)

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoi) in units of yg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each n	nethod as a	ppropriate into the	e yellow-shaded	d area, if no data	input data for each method as appropriate into the yellow-shaded area, if no data available leave blank					
Method	Matrix	Precision	Bias	Recovery	Recovery Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost Ease of Use	Ease of Use	OVERALL
reference		æ	R	æ	1/84	LoQ Requirement	UoM Requirement			RANKING
EN ISO 11885	ww	3.3		94.6	10	2	2	æ	00	35
EN ISO 18412	RW	6.4		5.86		2	2	566	00	35
EN 150 23913(FIA)	WM	55		66		2	2	666	00	25
EN ISO 23913(CFA)	WM	1.7		57.5		2	2	666	00	25
ISO 11083	¥	1.8		94.2		2	2	566	00	35
US EPA 200.8	¥	2.4		127.7	0.08	2	2	566	00	45
US EPA 200.7	ш	6.6		106	4	2	2	eee	00	45
						If 0, does not comply If 1, complies If 2, no LoQ requirement	If 0, does not comply If 1, complies If 2, no UoM requirement			

Input, as appropriate into the yellow-shaded area, the name of parameter

CHROMIUM

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yelliow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for eac	th method as	appropriate into t	he yellow-shad	ed area, if no data	input data for each method as appropriate into the yellow-shaded area, if no data available leave blank					
Method	Matrix	Precision	Bias	Recovery	Recovery Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
reference		æ	*	<i>8</i> 2	μς'	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of CLoI			ORDER
EN ISO 11885	WM	3.3		94.6	01	2	2	ecc	00	35
EN ISO 13386	WM	4.2		101.5	•	2	2	eee	00	25
EN 1233	WW	4.4		106.2		2	2	ecc t	00	35
ISO 9174	WM	4.4		106.2		2	2	EEE	00	35
150 17294	8	2.7		103.9		2	2	EEE	00	8
US EPA 6010C	ADW	8.4		100	4.7	2	2	EEE	00	35
US EPA 6020	AS	20				2	2	EEE	00	59
US EPA 200.7	ш	6.6		106	4	2	2	EEE	00	45
US EPA 200.8	¥	2.4		127.7	0.08	2	2	EEE	00	45
<b>MEWAM 163</b>	GW	5.7		92.6	0.06	2	2	ecc	00	45
						If 0, does not comply	If 0, does not comply			
						If 1, complies	If 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

Input, as appropriate into the yellow-shaded area, the name of parameter Non-organic

122

COBALT

Input, as appropriate into the yellow-shaded area, the critical level of interest (OLoI) in units of µg/I. This could be an EOS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank,

Input data for ead	h method as	Input data for each method as appropriate into the yellow-shaded area, if no	he yellow-shad	ed area, if no dat	i data available leave blank					
Method	Matrix	Precision	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM=3xs	Indicative cost Ease of Use	Ease of Use	OVERALL
reference		*	*	*	l∕s <del>u</del>	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of CLoI			ORDER
EN ISO 11885	WW	1.6		93.1	10	2	2	ЭЭЭ СЕСЕ	00	8
EN ISO 15586	WW	7		103	1	2	2	eee	00	35
ISO 17294	ង	3.7		96.8		2	2	ЭЭЭ	00	25
US EPA 6020A	Å	8.4				2	2	eee	00	65
US EPA 200.7	ш	11		8	2	2	2	eee	00	8
US EPA 200.8	ш	1.8		90.5	0:004	2	2	ЭЭЭ СЕСЕ	00	35
MEWAM 1638	SE	4.4		98.7	0.02	2	2	θŒ	0	25
						If 0, does not comply	If 0, does not comply			
						If 1, complies	If 1, complies			
						If 2, no LoQ requirement	If 2, no UoM requirement			

DW drinking water GW ground water RW river water

AS aqueous solution ReW reagent water

AdW acid-digested water

IE industrial effluent WW waste water

SE sewage effluent

SS synthetic standard U unknown

Non-organic

Input, as appropriate into the yellow-shaded area, the name of parameter 00

input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank	lethod as app	ropriste into the y	yellow-shaded al	rea, if no data a	ivailable leave blank					
Method reference Matrix	Matrix	Precision	Bias	Recovery	Recovery Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
		R	R	R	l/gm	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of CLoI			ORDER
150 6060	ш	3.4				2	2	EEE	00	22
ISO 13705	W	2.3			9	2	2	EEE	00	22
MEWAM 215 AB	ш	2.75	0.35			2	2	eee E	00	25
MEWAM 215 CDE	¥	1.4				2	2	eee E	000	7
US EPA 410.4	ReW	13.9		100.3		2	2	EEE	00	35
						If 0, does not comply If 1, complies If 2, no LoQ requirement	If 0, does not comply If 1, complies If 2, no UoM requirement			

Non-organic

Input, as appropriate into the yellow-shaded area, the name of parameter COPPER

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of Hg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank,

Input data for each	h method as a	appropriate into the	e yellow-shade	d area, if no data	Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank					
Method	Matrix	Precision	Bites	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
reference		×	æ	×	l/8H	LoQ Requirement 30 % of CLoI	UoM Requirement 50 % of CLOI			RANKING ORDER
EN ISO 11885	WM	1.4		97.3	01	2	2	eec	00	25
EN ISO 13386	WW	10		103	6.0	2	2	566	00	35
ISO 17294	55	3.4		100.3		2	2	566	00	25
150 8288	AS	3.9				2	2	555	00	22
US EPA 6020A	AS	16.6				2	2	666	00	99
US EPA 200.7	ш	1		102	m	2	2	666	00	25
US EPA 200.8	<u> </u>	2		92.5	0.02	2	2	55	00	8
US EPA 6010	ADW	17.7		96.7		2	2	666	00	35
<b>MEWAM 1638</b>	×	43		89.9	0.13	2	2	666	00	35
						If 0, does not comply	If 0, does not comply			

If 2, no UoM requirement If 1, complies

If 2, no LoQ requirement If 1, complies

Organic

Input, as appropriate into the yellow-shaded area, the name of parameter

DICHLOROMETHANE

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

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Input, as appropriate into the yelliow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

AA-EQS

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank	hethod as ap	propriate into the y	ellow-shaded a	area, ir no data a	vailable leave blank					
Method reference	Matrix	Precision	Bies	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost Ease of Use	Ease of Use	OVERALL
		R	R	R	Hg/I	LoQ, Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	30 % of CLOI			ORDER
EN ISO 10301 (I-I)	WW	11.8		133	30	•	1	5	00	57
EN ISO 10301 (HS)	WW	8.82		93.4	20	•	1	555	000	27
EN ISO 13680	GW	48.6		83	0.36	1	•	eee	000	22
MEWAM 170	GW	48.6		83	0.36	1	0	۲,	000	22
US EPA 324.2	ReW	53		66	0.03	1	1	666	000	25
US EPA 3030C	ReW	53		66	0.03	1	1	666	000	25
US EPA 8260	ReW	53		66	0.03	1	1	ecc	000	25
US EPA 624	э	32.4		68	2.8	•	•	666	000	8
US EPA 8020	AS	24.8		94.3	0.2	1	•	666	000	32
US EPA 8010	э	20.3		90		•	0	55	000	38
						If 0, does not comply	If 0, does not comply			

If 1, complies If 2, no UoM requirement

If 1, complies If 2, no LoQ, requirement

> DW drinking water GW ground water RW river water ReW reagent water AS aqueous solution AdW acid-digested water WW waste water E industrial effluent SE sewage effluent SS synthetic standard U unknown

Input, as appropriate into the yellow-shaded area, the name of parameter

Organic

126

ETHYLBENZENE

input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank	nethod as ap	propriate into the	yellow-shaded t	area, if no data a	vsijsbie jesve blank					
Method reference		Precision	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	
		R	æ	æ	н <b>5</b> /1	LoQ. Requirement 30 % of CLoI	UoM Requirement 50 % of CLoI			RANKING ORDER
EN ISO 15680	GW	63		101	0.17	2	2	909 666	000	24
EN ISO 11423-1	WW	36		113	2	2	2	eec	000	75
US EPA 602	AS	24.8		94.3	0.2	2	2	ecc	000	34
US EPA 342	Э	6.8		63		2	2	ecc	000	24
US EPA 302.2	ReW	14		101	0.01	2	2	999	000	24
US EPA 524.2	ReW	53		66	0.03	2	2	ecc	000	24
US EPA 3030C	ReW	53		66	0.03	2	2	555	000	24
US EPA 8260	ReW	5.3		66	0.03	2	2	ecc	000	24
US EPA 624	Э	24.4		100.5	7.2	2	2	555	000	31
US EPA 8020	AS	24.8		94.3	0.2	2	2	ecc	000	31
MEWAM 170	RW	10.2		103	0.13	2	2	ecc	000	34
EA-NLS FFP	ш	2		109	1	2	2	ecc	000	24
						If 0, does not comply	If 0, does not comply			

If 2, no UoM requirement

If 2, no LoQ requirement

If 1, complies

If 1, complies

DW drinking water GW ground water RW river water REW reagent water AS aqueous solution AdW waste water WW waste water IE industrial effluent SS synthetic standard U unknown

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Organic Input, as appropriate into the yellow-shaded area, the name of parameter

FLUORANTHENE

Input, as appropriate into the yellow-chaded area, the critical level of interest (CLof) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

0.0063

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data	thod as app	propriate into the ye	ellow-shaded at	rea, if no data av	available leave blank					
Method reference	Metrix	Precision	Bibs	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
		R	<i>.</i>	R	l/SH	LoQ. Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of CLoI			ORDER
EN ISO 28540 :2011	WW	10		86.8		•	1	eec	00	39
US EPA 610	ш	21.8		68	0.21	•	•	eec	00	28
US EPA 8100	Þ	21.8		68		•	•	eee	00	65
US EPA 8270 C &D	GW	22.4		82.1		•	•	eee	00	49
ISO 7981-2	22	13.8		93.2		•	1	eee	00	39
ISO 17993	DW	2.8		66	0.01	•	1	eee	00	28
<b>MEWAM 165</b>	GW	•		8	0.004	•	1	666	00	84
						If 0, does not comply If 1, complies	If 0, does not comply If 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

DW drinking water GW ground water RW river water ReW resgent water AS aqueous solution AdW acid-digested water WW waste water WW waste water E industrial effluent SE sewage effluent SS synthetic standard U unknown

Non-organic

Input, as appropriate into the yellow-shaded area, the name of parameter

FLUORIDE

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank	nethod as app	vropriste into the ye	ilow-shaded at	rea, if no data av	vaijable leave blank					
Method reference	Matrix	Precision	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
		æ	2	R	Hg/I	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of Cloi	50 % of CLoI			ORDER
EN ISO 10304-1	22	2.7		103		2	2	eee	000	24
ISO 10339-1	DW	4.1		81.6	20	2	2	eee	000	34
ISO 10339-2	WW	11.7		99.2	200	2	2	eee	000	34
US EPA 300.1	GW	0.85		84.3		2	2	566	000	34
US EPA 340	5	14.1		103	100	2	2	566	000	34
US EPA 9056	WW	11		92		2	2	566	000	34
						If 0, does not comply If 1, complies	If 0, does not comply If 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

DW drinking water GW ground water RW river water ReW reagent water AdW acid-digested water WW waste water

SS synthetic standard

U unknown

SE sewage effluent

IE industrial effluent

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## Non-organic

Input, as appropriate into the yellow-shaded area, the name of parameter

# FREE CVANIDE

input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for e	cach me	ethod as ap	propriate into the	yellow-shaded a	area, if no data a	input data for each method as appropriate into the yellow-shaded area, if no data available leave blank					
Method reference	an ce	Matrix	Precision	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
			R	æ	R	Hg/I	LoQ Requirement	<b>UoM Requirement</b>			RANKING
							30 % of CLoI	50 % of CLoI			ORDER
EN ISO 14403		WM	1.33		105		2	2	eec	0	26
150 6703		GW	19				2	2	eec	0	99
<b>MEWAM 235</b>	A1	Soil	13.3		111.5		2	2	eec	0	46
<b>MEWAM 235</b>	A2	Soil	3.7	-2.1			2	2	eec	0	26
<b>MEWAM 235</b>	A3	Soil	5	-18.9			2	2	555	٥	36
							If 0, does not comply	If 0, does not comply			
							If 1, complies	If 1, complies			
							If 2, no LoQ requirement	If 2, no UoM requirement			

AdW acid-digested water AS aqueous solution IE industrial effluent ReW reagent water SE sewage effluent DW drinking water GW ground water WW waste water RW river water

SS synthetic standard

U unknown

Input, as appropriate into the yellow-shaded area, the name of parameter

Organic

NDENO(1,2,3-cd)PYRENE

input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/1. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank. 0.00017

input, as appropriate into the yellow-chaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

#### AA-EQS

input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

Method reference	Matrix	Precision %	Si as	Recovery %	Limit of detection µg/1	LoQ = 3 x LoD LoQ Requirement 30 % of CLoI	UoM = 3 x s UoM Requirement 50 % of CLoI	Indicative cost	Ease of Use	OVERALL RANKING ORDER
EN ISO 28540 :2011	WW	6.9		64.4		•	1	eee	00	49
US EPA 610	ш	22.7		z	0.043	•	•	ecc	00	58
US EPA 8100	Э	22.7		89		•	•	eee	00	<mark>65</mark>
US EPA 8270 C &D	GW	37		74.9		•	•	ecc	00	69
ISO 7981-3	22	12.2		93.6		•	1	eee	00	39
ISO 17993	DW	•		57.5	0.01	•	1	EEE	00	28
<b>MEWAM 165</b>	GW	2		82	0.006	0	1	eee	00	38
						If 0, does not comply	If 0, does not comply			

If 1, complies If 2, no UoM requirement

If 1, complies If 2, no LoQ requirement

> DW drinking water GW ground water RW river water ReW resent water AS aqueous solution AW waste water WW waste water E industrial effluent SE sewage effluent SS synthetic standard U unknown

Input, as appropriate into the yellow-shaded area, the type of analysis as Organic or Non-organic <mark>Non-organic</mark>

Input, as appropriate into the yellow-shaded area, the name of parameter

IRON

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/I. This could be an EOS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EOS value, permit concentration, process control level or other. If none, leave blank

Input data for each	h method as a	appropriate into the	e yellow-shade	d area, if no dat	Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank					
Method	Matrix	Precision	Bias	Recovery	Limit of detection	$LoQ = 3 \times LoD$	UoM=3xs	Indicative cost Ease of Use	Ease of Use	OVERALL
reference		29	8	8	Lar He	LoQ, Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of CLoI			ORDER
EN ISO 11885	WW	1.8		8		2	2	æ	00	8
EN ISO 15586	ង	3.4		001	1	2	2	æ	00	22
US EPA 6020A	SA	80.5				2	2	æ	00	75
US EPA 200.7	ш	11.5		93.5	8	2	2	W	00	45
US EPA 6010	AdW	63		57.7	41	2	2	θŒ	00	8
MEWAM 76	DW	15.8		102	8	2	2	æ	00	85
						If 0, does not comply	If 0, does not comply			
						If 1, complies	lf 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

DW drinking water GW ground water RW river water ReW reagent water AS aqueous solution AdW waste water AdW waste water AdW waste effluent E industrial effluent SE sewage effluent SE synthetic standard U unknown

ea, the type of analysis as Organic or Non-organic	
e yellow-shaded ar	
Input, as appropriate into th	Non-organic

Input, as appropriate into the yellow-shaded area, the name of parameter

KJELDAHL NITROGEN

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Method reference	Matrix	Precision	Bibs	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
		R	R	R	I/SH	LoQ Requirement 30 % of CLoI	UoM Requirement 50 % of CLol			RANKING ORDER
EN 23663	ш	0.64			1000	2	2	999 EEE	00	55
ISO 3663	ш	0.64			1000	2	2	666	00	55
MEWBAM 126	SS	1.7			1000	2	2	eee	80	55
						If 0, does not comply	If 0, does not comply			
						If 1, complies	If 1, complies			
						If 2, no LoQ requirement	If 2, no UoM requirement			
DW drinking water										
<b>GW ground water</b>										

AdW acid-digested water

IE industrial effluent

WW waste water

AS aqueous solution

ReW reagent water

RW river water

SS synthetic standard

U unknown

SE sewage effluent

Non-organic

Input, as appropriate into the yellow-shaded area, the name of parameter

LEAD

input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

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Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

AA-EOS

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

Method	Matrix	Precision	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost Ease of Use	Ease of Use	OVERALL
reference		æ	*	æ	He'l	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of Cloi	50 % of CLoI			ORDER
EN ISO 11885	WM	2.9		89.7	200	•	1	999	00	38
EN ISO 13386	8	5.6		102	1	•	1	999	00	38
EN ISO 17294	8	4		107.2		•	1	999	00	39
150 8288-1	\$¥	7.9				•	1	999	00	69
US EPA 6020A	AS	17				•	•	999	00	69
US EPA 200.7	ш	12.5		84	10	•	1	ecc	00	48
US EPA 200.8	ш	2.1		108.4	0.05	1	1	666	00	36
US EPA 6010	AdW	20.7		106.3		•	•	666	00	59
<b>MEWAM 163</b>	×	5.4		97	0.02	1	1	666	00	36
						If 0, does not comply	If 0, does not comply			
						If 1, complies	If 1, complies			
						If 2, no LoQ requirement	If 2, no UoM requirement			

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Non-organic

Input, as appropriate into the yellow-shaded area, the name of parameter

MANGANESE

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each	method as a	ppropriate into the	e yellow-shader	d area, if no data	input data for each method as appropriate into the yellow-shaded area, if no data available leave blank					
Method	Matrix	Precision	Bies	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
reference		æ	æ	æ	HS/I	LoQ Requirement 30 % of CLoI	UoM Requirement 50 % of CLoI			RANKING ORDER
EN ISO 11885	WM	13		1.96		2	2	999	00	22
EN ISO 13386	WW	4.3		111	0.5	2	2	eee	00	35
EN ISO 17294	55	3.2		98.2		2	2	ecc	00	22
US EPA 200.7	ш	6.6		68	1	2	2	ecc	00	45
US EPA 200.8	ш	3.7		103.6	0.02	2	2	ecc	00	22
MEWAM 76	ΝQ	29.3		102	10.8	2	2	999	00	45
<b>MEWAM 1638</b>	35	4.2		97.3	0.04	2	2	999	00	25
						If 0, does not comply If 1, complies	If 0, does not comply If 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

DW drinking water GW ground water RW river water ReW reagent water AS aqueous solution AdW acid-digested water WW waste water IE industrial effluent SE sewage effluent SS synthetic standard U unknown

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Von-organic

Input, as appropriate into the yellow-shaded area, the name of parameter

MERCURY

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/I. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank:

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

If 2, no UoM requirement

If 2, no LoQ requirement

If 1, complies

If 1, complies

DW drinking water GW ground water RW river water ReW resgent water AdW vaste water WW waste water IE industrial effluent SE sewage effluent SS synthetic standard U unknown

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Input, as appropriate into the yellow-shaded area, the name of parameter

MTBE

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

	OVERALL	RANKING	ORDER	54	77	4	54	21	
	Ease of Use			000	000	000	000	000	
	Indicative cost			666	666	999	ecc	999	
	UoM = 3 x s	<b>UoM Requirement</b>	50 % of CLoI	2	2	2	2	2	If 0, does not comply If 1, complies
	LoQ = 3 x LoD	LoQ Requirement	30 % of CLoI	2	2	2	2	2	If 0, does not comply If 1, complies
available leave blank	Limit of detection	He'		0.2		12	0.3	2.28	
d area, if no data	Recovery	R		100.5	101	130	97.1	101	
the yellow-shade	Bias	R							
ppropriate into t	Precision	R		5.6	51	3.6	6.76	5.45	
nethod as a	Matrix			GW	5	ReW	ш	ш	
Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank	Method reference Matrix			MEWAM 170	US EPA 8260	US EPA 324.2	EA -NLS MCERTS	EA -NLS FFP	

If 2, no UoM requirement

If 2, no LoQ requirement

DW drinking water GW ground water RW river water ReW reagent water AS aqueous solution AdW acid-digested water AdW waste water IE industrial effluent SE sewage effluent SS synthetic standard U unknown

## Organic

Input, as appropriate into the yellow-shaded area, the name of parameter

# NAPHATHALENE

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

### AA-EQS

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

Method reference Matrix Precision Bias Recovery Limit of detection LoQ = 3 x LoD

RANKING	<b>49</b>	58	<mark>29</mark>	<b>49</b>	22	26	46	27	
	00	00	00	00	000	00	00	000	
	ecc	ecc	ecc	ecc	ecc	eee	666	666	
UoM Requirement 50 % of CLoI	1	•	•	•	1	1	1	1	If 0, does not comply If 1, complies
LoQ Requirement 30 % of CLoI	•	•	•	•	1	1	1	•	If 0, does not comply If 1, complies
I/SH		1.8			0.004	0.01	0.004	1.4	
R	35.2	56.3	56.3	37.16	104	66	8	98	
×									
×	6.7	24.4	24.4	22.6	8.2	2.8	•	9.7	
	WW	ш	э	GW	ReW	22	GW	GW	
	EN ISO 28540 :2011	US EPA 610	US EPA 8100	US EPA 8270 C &D	US EPA 324	ISO 17993	<b>MEWAM 165</b>	ISO 13680	

If 2, no UoM requirement

If 2, no LoQ requirement

DW drinking water GW ground water RW river water ReW reagent water AS aqueous solution AdV acid-digested water WW waste water IE industrial effluent SE sewage effluent

SS synthetic standard

U unknown

OVERALL

Ease of Use

Indicative cost

UoM = 3 x s

input, as appropriate into the yellow-shaded area, the name of parameter

Non-organic

NICKEL

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

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Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank. AA-EOS

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

Method reference	Matrix	Precision	Bias	Recovery	Recovery Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost Ease of Use	Ease of Use	OVERALL
		R	R	R	I/BH	LoQ Requirement 30 % of CLoI	UoM Requirement 50 % of CLoI			RANKING
US EPA 6020A		6.4			0.03	1	-1	666	000	8
US EPA 6010C	AdW	10.3		94.3	10	•	1	666	000	47
ISO 11885	WW	1.6		92.1		•	1	666	000	ŝ
US EPA 200.8	51	4.1		97.8	0.06	1	1	666	000	25
US EPA 200.7	5	2		92.5		•	1	666	000	37
MEWAM 45	DW	2.8			4.3	•	1	ecc	000	57
MEWAM 163	25	4.8		16	0.13	1	1	eee	000	35
150 8288	ReW	m				•	1	666	000	22
EN ISO 13386	WW	4.2		66	1	•	1	666	000	26
ISO 17294	ន	43		86		•	1	ecc	000	28
						If 0, does not comply	If 0, does not comply			
						If 1, complies	If 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

AdW acid-digested water SS synthetic standard AS aqueous solution IE industrial effluent ReW reagent water SE sewage effluent DW drinking water GW ground water WW waste water RW river water U unknown

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AdW acid-digested water

IE industrial effluent SE sewage effluent

WW waste water

AS aqueous solution

ReW reagent water

RW river water

DW drinking water GW ground water SS synthetic standard

U unknown

analysis as Organic or Non-organic	
ellow-shaded area, the type of	
Input, as appropriate into the y	Non-organic

Input, as appropriate into the yellow-shaded area, the name of parameter

NITRATE

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yelliow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank	hethod as app	propriate into the y	reliow-shaded an	rea, if no data a	ivailable leave blank					
Method reference Matrix	Matrix	Precision	Bibs	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
		æ	×	R	I/SH	LoQ Requirement 30 % of CLoI	UoM Requirement 50 % of CLOI			RANKING ORDER
EN ISO 10304-1	22	1.6		103		2	2	eee	000	24
EN ISO 10304-2	ш	55		99.7		2	2	ecc	000	24
ISO 7890-3	RW	2.6				2	2	eee	000	2
US EPA 300	GW	0.27		96.3		2	2	ecc	000	24
US EPA 9056	WW	3		94.3		2	2	ecc	000	34

If 2, no UoM requirement

If 2, no LoQ requirement

If 0, does not comply If 1, complies

If 0, does not comply If 1, complies

## concawe

Input data for each method as appropriatelinto the velow-shaded area. If no data available leave blant	ethod as app	propriatelinto the ve	ellow-shaded an	ea. if no data a	vsijsbie leave blank					
Method reference	Matrix	Precision	Bites	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
		R	æ	æ	I/SH	LoQ Requirement 30% of Clot	UoM Requirement so % of Clot			RANKING
EN ISO 10304-1	22	1.6		103		2	2	555	000	24
EN ISO 10304-2	ш	1.81		102.3		2	2	ecc	000	24
EN ISO 13395 (FIA)	ш	5.9		102.7		2	2	566	000	34
EN ISO 13395 (CFA)	ш	10.3		112.3		2	2	eee	000	44
US EPA 300	GW	0.77		36.6		2	2	ecc	000	34
US EPA 9036	WM	2		100		2	2	666	000	24

input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, the type of analysis as Organic or Non-organic

input, as appropriate into the yellow-shaded area, the name of parameter

Non-organic

VITRITE

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

If 2, no UoM requirement

If 2, no LoQ requirement

If 0, does not comply If 1, complies

If 0, does not comply If 1, complies

DW drinking water GW ground water RW river water ReW regent water AdW vaste water WW waste water IE industrial effluent SS synthetic standard
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ak.		Ease of use OVERALL RANKING
rol level, etc. If none, leave bia		Indicative cost Ease
concentration, or a process control level, etc. If none, leave blank.	one, lesve blank.	VoM = 3 x s VoM Requirement

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ut, as appropriate into the yellow-shaded area, the type of analysis as Organic or Non-orga
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# Organic

input, as appropriate into the yellow-shaded area, the name of parameter

# PENTACHLOROBENZENE

input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit of 0.007

input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If noi AA-EQS

# input deta for each method as appropriate into the yellow-shaded area, if no data available leave blank

Method reference		Precision	10 M	Recovery	tecovery Limit of detection % µg/)	LoQ = 3 x LoD LoQ Requirement 30 % of CLoi	UoM = 3 x s UoM Requirement 50 % of CLot	Indicative cost	st Ease of Use
EN ISO 6468				86.2	10000	0		8	0
US EPA 342	(MS)	4.7		2.64		0	1	8	0.0
						If 0, does not comply If 1, complies	If 0, does not comply If 1, complies		

If 2, no UoM requirement

If 2, no LoQ, requirement

ORDER 39 22

### AdW acid-digested water AS aqueous solution IE industrial effluent ReW reagent water DW drinking water **GW ground water** WW waste water RW river water

SS synthetic standard

U unknown

SE sewage effluent

Input, as appropriate into the yellow-shaded area, the name of parameter Non-organic

PHOSPHATE

input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank 1 

se OVERALL RANKING ODDEP	44	24	24	4	
Ease of Use	000	000	000	000	
Indicative cost	eee	eec	eec	eee	
UoM = 3 x s UoM Requirement so % of Cod	2	2	2	2	If 0, does not comply If 1, complies
LoQ = 3 x LoD LoQ Requirement ao % of Clot	2	2	2	2	If 0, does not comply If 1, complies
Limit of detection µg/1				3400	
Recovery %	6	96.1	86		
sa Bi				-10.2	
Matrix Precision	8.4	4.19	1	12.7	
Metrix	S	ш	WW	WW	
Method reference	EN ISO 10304-1	EN ISO 10304-2	EN ISO 13681	SM 4110B	

If 2, no UoM requirement

If 2, no LoQ requirement

AdW acid-digested water SS synthetic standard AS aqueous solution IE industrial effluent ReW reagent water SE sewage effluent DW drinking water GW ground water WW waste water RW river water U unknown

ea, the type of analysis as Organic or Non-organic		
Input, as appropriate into the yellow-shaded an	Non-organic	

Input, as appropriate into the yellow-shaded area, the name of parameter

## SELENIUM

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for eac	th method as	appropriate into th	he yellow-shade	ed area, if no dat	input data for each method as appropriate into the yellow-shaded area, if no data available leave blank					
Method	Matrix	Precision	Bies	Recovery	Recovery Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
reference		æ	æ	æ	μ¢,	LoQ. Requirement 30 % of CLoI	UoM Requirement 50 % of CLoI			RANKING ORDER
EN ISO 11885	ww	2		2.99	0.1	2	2		0.0	26
EN ISO 13386	WW	9.8		100		2	2	ecc	0 0	35
2965 OSI	ww	11.2		86.2		2	2	ecc	0 0	45
150 17379-1	WW	m		101.4		2	2	eee tee	00	25
150 17379-2	ш	3.4		98.1		2	2	EEE	00	25
US EPA 6020A	AS	20				2	2		00	99
US EPA 6010	AdW	24.1		102.3	90	2	2	EEE	00	45
US EPA 200.8	ш	3.6		123.9	2.1	2	2		00	56
						If 0, does not comply	If 0, does not comply			

If 1, complies If 2, no UoM requirement

If 1, complies If 2, no oOQ requirement

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Input, as a	Non-oras

Input, as appropriate into the yellow-shaded area, the name of parameter

# SULPHATE

input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

	OVERALL	RANKING	ORDER	24	54	7	4	
	Ease of Use			000	000	000	000	
	Indicative cost			eec	EEE	eee	EEE	
	UoM = 3 x s	<b>UoM Requirement</b>	50 % of Clot	2	2	2	2	If 0, does not comply
	LoQ = 3 x LoD	LoQ Requirement	30 % of CLoI	2	2	2	2	If 0, does not comply
Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank	Recovery Limit of detection	He/				10000	5800	
ed area, if no data	Recovery	R		100.1	101			
the yellow-shad	Bias	R					-14.7	
ppropriate into	Precision	R		2	2.15	1	13.7	
method as a	Matrix			8	ш	5	WW	
Input data for each r	Method reference Matrix			EN ISO 10304-1	EN ISO 10304-2	150 9280	SM 4110B	

If 1, complies If 2, no UoM requirement

If 2, no LoQ requirement

If 1, complies

DW drinking water GW ground water RW river water ReW reagent water AS aqueous solution AdW acid-digested water WW waste water WW waste water E industrial effluent SS synthetic standard U unknown

Non-organic

SULPHIDE

Input, as appropriate into the yellow-shaded area, the name of parameter

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

OVERALL RANKING ORDER		54	54	4		
Ease of Use	000	000	000	0000		
Indicative cost Ease of Use	ecc	ecc	ecc	555		
UoM = 3 x s UoM Requirement 30 % of CLoI	2	2	2	2	lf 0, d lf lf 2, no l	
LoQ = 3 x LOD LoQ Requirement 30 % of CLoI	2	2	2	2	If 0, does not comply If 1, complies If 2, no LoQ requirement	
Limit of detection µg/l		260	m			
Recovery %	51					
in an				-6.1		
Precision %	1.8	21	11	60		
Metrix	5	ш	22	22		
Method reference Matrix	150 10530	MEWAM 73A	MEWAM 73B	<b>MEWAM 228B</b>		DW drinking water GW ground water

AdW acid-digested water

IE industrial effluent

WW waste water

AS aqueous solution

ReW reagent water

RW river water

SS synthetic standard

U unknown

SE sewage effluent

Non-organic
Input, as appropriate into the yellow-shaded area, the name of parameter
SUPHITE
Input, as appropriate into the yellow-shaded area, the critical level of interest (CLOI) in units of ug/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.
Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Method reference Matrix Precision Bias Recovery Limit or detection % % % % % w yus// 150 10304-3 16 3.32 SM 4700 16 8							
% 150 10304-3 1E 3.32 SM 4300 1E E 8	Bias Recovery	rery Limit of detection	LoQ = 3 x LoD	UoM = 3 X 5	Indicative cost Ease of Use	Ease of Use	OVERALL
150 10304-3 IE 3.32 SM 4300 IE E	<i>a</i> <i>a</i>	1/SH	LoQ, Requirement 30 % of CLoI	UoM Requirement 50 % of CLOI			ORDER
SM 4500 IE 8			2	2	ecc	000	3
			2	N	eec.	000	54
			If 0, does not comply If 1, complies	If 0, does not comply If 1, complies			
			If 2, no LoQ requirement	If 2, no LoQ requirement If 2, nNo UoM requirement			

AdW acid-digested water SS synthetic standard U unknown AS aqueous solution IE industrial effluent ReW reagent water DW drinking water GW ground water SE sewage effluent WW waste water RW river water

Organic

Input, as appropriate into the yellow-shaded area, the name of parameter

TETRACHLOROETHYLENE

input, as appropriate into the yellow-chaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. if none, leave blank. 9

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

AA-EQS

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank. Method reference Methic Bracition Bise Bise

Method reference Matrix	Precision %	ie: %	Recovery %	Limit of detection µ5/1	LoQ = 3 × LoD LoQ Requirement 30 % of CLoI	UoM = 3 x s UoM Requirement 50 % of CLol	Indicative cost Ease of Use	Ease of Use	OVERALL RANKING ORDER
WW	7.8		101	0.1	1	1	*	00	25
WW	17.6		45.7	0.2	1	•	*	000	54
ΒŴ	4		102	0.12	1	1	*	000	24
GW	4		102	0.12	1	1	5	000	24
RW	21.2		100	1.6	•	•	8	000	8
ReW	6.8		63	0.14	1	1	8	000	
ReW	19.3		56	0.001	1	•	8	000	34
ш	5.31		113	0.5	1	1	8	000	쳤
					If 0, does not comply If 1, complies	If 0, does not comply If 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

DW drinking water GW ground water RW river water ReW reagent water AdW acid-digested water WW waste water E industrial effluent SS synthetic standard U unknown

corganic or Non-organic		5
the type of analysis as		the name of parametr
yellow-shaded area,		yellow-shaded area,
input, as appropriate into the	Non-organic	Input, as appropriate into the

input, as appropriate into the yellow-shaded area, the critical level or interest (CLoI) in units of ug/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank: ŭ

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

input data for each method as appropriate into the yeilow-shaded area, if no data available leave blank

Aethod reference	ce Matrix P	Precision	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost Ease of Use	Ease of Use	OVERALL
		8	R	R	1/Sm &	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLot	50 % of CLOI			ORDER
11484	2	29		116.6		2	2	eee	9.0	35
EWAM 157	GW	10.7			200	2	2	ter	9.6	65
TEWAM 157 (UV)	GW	42			50	2	2	CCC.	000	25
						If 0, does not comply	If 0, does not comply			
						If 1, complies	If 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

AdW acid-digested water SS synthetic standard AS aqueous solution **ReW reagent water** IE industrial effluent SE sewage effluent. DW drinking water **GW ground water** WW waste water RW river water.

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Part 1

Organic

Input, as appropriate into the yellow-shaded area, the name of parameter

TOLUENE

input, as appropriate into the yellow-shaded area, the critical level of interest (CLof) in units of ug/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if	nethod as app	ropriste into the y	ellow-shaded a	rea, if no data av	no data available leave blank					
Method reference	Matrix	Precision	Bias	Recovery	Recovery Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	
		R	R	8	19 1	LoQ. Requirement	<b>UoM Requirement</b>			
						30 % of CLoI	50 % of CLoI			RANKING ORDER
EN ISO 15680	GW	3		101	0.1	2	2	5	000	24
EN ISO 11423-1	ww	12.1		119.8	2	2	2	te te	000	4
US EPA 602	AS	17.7		94.7	0.2	2	2	eee eee	000	쿪
US EPA 342	5	6.5		86		2	2	eee eee	000	24
US EPA 302.2	ReW	0.8		66	0.01	2	2	eee eee	000	24
US EPA 524.2	ReW	6.6		102	0.08	2	2	55	000	24
US EPA 3030C	ReW	6.6		100	0.08	2	2	eee Gee	000	24
US EPA 8260	ReW	6.5		100	0.08	2	2	666	000	24
US EPA 624	5	17.7		100	9	2	2	ecc	000	31
US EPA 8020	AS	17.7		94.7	0.2	2	2	eee eee	000	31
MEWAM 170	RW	8.8		103.8	0.15	2	2	55	000	24
EA-NLS FFP	ш	3.14		111	0.2	2	2	eee	000	*
						If 0, does not comply If 1, complies	If 0, does not comply If 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

DW drinking water GW ground water RW river water RW river water AS aqueous solution AdW acid-digested water WW waste water UW waste effluent SE sewage effluent SS synthetic standard U unknown

Input, as appropriate into the yellow-shaded area, the type of analysis as Organic or Non-organic Non-organic	e into the ye	illow-shaded area,	, the type of and	ysis as Organic o	ər Nan-organic					
input, as appropriate into the yellow-shaded area, the name of parameter	e into the ye	mow-shaded area.	, the name of pa	rameter						
TOTAL SUSPENDED SOUDS	soups									
input, as appropriat	e into the ye	Mow-shaded area	, the critical leve	I of interest (CLoI	I) in units of µg/L This cout	input, as appropriate into the yellow-shaded area, the critical level of interest (CLoi) in units of Jg/L This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank	Icentration, or a process control	Hevel, etc. If none, le	ave bisnk.	
input, as appropriat	e into the ye	inow-shaded area	, whether this is	an EQS value, pe	rmit concentration, proce	input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.	e, leave blank.			
input data for each	method as a	opropriete into th	te yellow-shaded	area, if no data a	Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank					
Method reference	Matrix	Precision	Bibs	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 K 5	Indicative cost	Ease of Use	OVERALL
		R	×	æ	1/511	LoQ Requirement 30 % of CLoi	UoM Requirement 50 % of CLoi			RANKING
EN ISO 872	n	43			2000	2	2	eec	000	24
(SO 11923	a	54			2000	2	2	eec.	000	24
EA-WLS FFP	E	m				2	2	ter	000	2

If 1, complies If 2, no UoM requirement If 0, does not comply N

> If 1, complies If 2, no LoQ, requirement if 0, does not comply

DW drinking water	GW ground water	RW river water.	ReW reagent water	AS aqueous solution	AdW acid-digested water	WW waste water	E industrial effluent	SE sewage effluent	SS synthetic standard

U unknown

Input, as appropriate into the yellow-shaded area, the name of parameter

TOTAL NITROGEN

input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank Mathod attenance Mathin Descriptor Bird Bacouster Limit of dataction 100 - 3 v 100

Method reference	Matrix	Precision	Bias	Recovery	Limit of detection		UoM = 3 x s	Indicative cost Ease of Use	Ease of Use	OVERALL
		R	R	R	l∕∎		<b>UoM Requirement</b>			RANKING
							50 % of CLoI			ORDER
EN 23663	ш	0.64			1000	2	2	666	00	8
ISO 3663	ш	0.64			1000		2	55	00	8
EN 12260	WW	1.6		5126	300	2	2	55	000	24
EN ISO 13395 (FIA)	WW	1.6		101.5		2	2	55	000	24
EN ISO 13395 (CFA)	WW	2.7		104		2	2	ecc tec	000	24
EN ISO 11732 (FIA)	ReW	2.1				2	2	666	000	7
EN ISO 11732 (CFA)	ReW	12				2	2	555	000	7
EN ISO 11905-1	ш	1.96		98	20	2	2	566	000	54
ISO 6777	ш	2		99.7		2	2	566	000	21
						If 0, does not comply	If 0, does not comply			
						If 1. complies	If 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

DW drinkling water GW ground water RW river water ReW reagent water AdW acid-digested water WW waste water WW waste water IE industrial effluent SE synthetic standard U unknown \* \* \* \*

If 2, no UoM requirement

If 2, no LoQ requirement

If 1, complies

If 1, complies

If 0, does not comply

If 0, does not comply

N

ISO 15681-2

N

Input, as appropriate into the yellow-shaded area, the type of analysis as Organic or Non-organic

Input, as appropriate into the yellow-shaded area, the name of parameter

TOTAL PHOSPHORUS

Non-organic

DW drinking water	GW ground water	RW river water	ReW reagent water	AS aqueous solution	AdW acid-digested water	WW waste water	IE industrial effluent	SE sewage effluent

SS synthetic standard

U unknown

Organic

Input, as appropriate into the yellow-shaded area, the name of parameter

TRICHLOROMETHANE

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yelliow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

AA-EQS

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

Method reference	Matrix	Precision	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost Ease of Use	Ease of Use	OVERALL
		R	æ	æ	Hg/I	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of AA-EQS			ORDER
EN ISO 10301 (L-L)	WM	53				0	1	8	00	28
EN ISO 10301 (HS)	WW	2.9		78.9	0.2	1	1	8	000	쳤
EN ISO 13680	GW	6.5		100	0.1	1	1	8	000	24
MEWAM 170	GW	53		100	0.1	1	1	5	000	54
MEWAM 110	RW	13.8		105	0.66	•	1	8	000	35
US EPA 524.2	ReW	7.3		96	0.19	1	1	#	000	24
US EPA 8010	ReW	17.6		55	0.002	1	•	÷	000	뷺
US EPA 3030C	ReW	m		105	0.04	1	1	¥	000	22
US EPA 624	WW	16.9		93.3	1.6	0	•	#	000	뷺
EA-NLS FFP	¥	7.05		110	11	0	1	5	000	24
						If 0, does not comply	If 0, does not comply			

If 1, complies If 2, no UoM requirement

If 1, complies If 2, no LoQ requirement

> DW drinking water GW ground water RW river water AS aqueous solution AdW acid-digested water WW waste water E industrial effluent SE synthetic standard U unknown

VANADIUM

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/I. This could be an EOS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EOS value, permit concentration, process control level or other. If none, leave blank

	OVERALL	RANKING	ORDER	54	54	34	4	74	24		
	Ease of Use			000	000	000	000	000	000		
	Indicative cost			θŒ	eee	eee	eee	eee	<del>ecc</del>		
	UoM=3xs	<b>UoM Requirement</b>	50 % of CLoI	2	2	2	2	2	2	If 0, does not comply	If 1, complies
	LoQ=3x LoD	LoQ, Requirement	30 % of CLoI	2	2	2	2	2	2	If 0, does not comply	If 1, complies
Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank	Limit of detection	E C		2		e	0.9	0.03	2		
ded area, if no dat	Recovery	8		102	6'16	87	75.5		<u>99.3</u>		
othe yellow-shad	Bias	8									
appropriate into	Precision	*		11	4.7	1.25	0.05	45.5	1.9		
th method as :	Matrix			WW	ង	<b>=</b>	ш	SA	AdW		
Input data for eac	Method	reference		EN ISO 15586	ISO 17294	US EPA 200.7	US EPA 200.8	US EPA 6020A	US EPA 6010C		

If 2, no UoM requirement

If 2, no LoQ requirement

AdW acid-digested water SS synthetic standard U unknown AS aqueous solution IE industrial effluent ReW reagent water SE sewage effluent DW drinking water **GW ground water** WW waste water RW river water

ellow-shaded area, the type of analysis as Organic or Non-organic	
Input, as appropriate into the y	Organic

Input, as appropriate into the yellow-shaded area, the name of parameter

## m-XYLENE

input, as appropriate into the yellow-shaded area, the critical level of interest (CLoi) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yelliow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

Method reference	Matrix	Precision	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	
		æ	æ	æ	l/BH	LoQ. Requirement 30 % of CLOI	UoM Requirement 50 % of CLoI			
US EPA 302.2	ReW	1.4		100	0.01	2	2	3		
US EPA 524.2	ReW	3		97	0.03	2	2	5	000	
US EPA 5030C	ReW	3		57	0.03	2	2	55		
US EPA 8260	ReW	3		25	0.03	2	2	5		
US EPA 8021	AS			100	0.01	2	2	æ		

OVERALL RANKING ORDER

ននន ន

If 2, no UoM requirement

If 2, no LoQ requirement If 0, does not comply If 1, complies

If 0, does not comply If 1, complies

AdW acid-digested water AS aqueous solution IE industrial effluent ReW reagent water DW drinking water GW ground water WW waste water RW river water

SS synthetic standard

U unknown

SE sewage effluent

Input, as appropriate into the yellow-shaded area, the name of parameter

Organic

0- XYLENE

Input, as appropriate into the yelliow-shaded area, the critical level of interest [CLoI] in units or µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yelliow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank

Input to a to a country		Sin our state lide ide	Venue Allance		inper user to com interiou as appropriate into are yeared at co. In no data available react picture					
Method reference		Precision	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost Ease of Use	Ease of Use	
		×	×	R	l/8H	LoQ Requirement	<b>UoM Requirement</b>			
						30 % of CLoI	50 % of CLoI			RANKING ORDER
EN ISO 13680	GW	4.7		105	60.0	2	2	eee	000	24
EN ISO 11423-1	WW	10		91.7	2	2	2	ecc CCC	000	24
US EPA 342	5	7.2		66		2	2	eee eee	000	24
US EPA 302.2	ReW	0.8		66	0.02	2	2	eee	000	24
US EPA 324.2	ReW	7.2		103	0.06	2	2	ecc	000	24
US EPA 3030C	ReW	7.2		103	0.06	2	2	566	000	24
US EPA 8260	ReW	7.2		103	0.06	2	2	999	000	24
US EPA 8021	AS			66	0.01	2	2	999	000	51
MEWAM 170	RW	53		102.9	0.13	2	2	666	000	24
ES-NLS FFP	ш	4.95		109	6.9	2	2	eee eee	000	24
						If 0, does not comply	If 0, does not comply			

If 1, complies If 2, no UoM requirement

If 1, complies If 2, no LoQ requirement

> DW drinking water GW ground water RW river water ReW reagent water AS aqueous solution AdW acid-digested water WW waste water IE industrial effluent SE synthetic standard U unknown

Organic

Input, as appropriate into the yellow-shaded area, the name of parameter

p-XYLENE

Input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of µg/L. This could be an EQS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank.

Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank 

Method reference	Matrix	Precision	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM = 3 x s	Indicative cost	Ease of Use	OVERALL
		*	æ	R	I/BH	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of Cloi			ORDER
US EPA 302.2	ReW	6.0		65	0.02	2	2	8	000	23
US EPA 524.2	ReW	2.7		104	0.06	2	2	8	000	23
US EPA 3030C	ReW	2.7		104	0.06	2	2	8	000	23
US EPA 8260	ReW	2.7		104	0.06	2	2	8	000	23
						If 0, does not comply If 1, complies	If 0, does not comply If 1, complies			

If 2, no UoM requirement

If 2, no LoQ requirement

AdW acid-digested water SS synthetic standard AS aqueous solution IE industrial effluent ReW reagent water SE sewage effluent DW drinking water GW ground water WW waste water **RW river water** U unknown

Non-organic Input, as appropriate into the yellow-shaded area, the name of parameter

ZINC

input, as appropriate into the yellow-shaded area, the critical level of interest (CLoI) in units of Hg/I. This could be an EOS value, a permit concentration, or a process control level, etc. If none, leave blank.

Input, as appropriate into the yellow-shaded area, whether this is an EQS value, permit concentration, process control level or other. If none, leave blank

Input data for ead	h method as	appropriate into t	the yellow-shad	led area, if no dat	Input data for each method as appropriate into the yellow-shaded area, if no data available leave blank					
Method	Matrix	Precision	Bias	Recovery	Limit of detection	LoQ = 3 x LoD	UoM=3xs	Indicative cost	Ease of Use	PRIORITISED
reference		*	8	8	1 H	LoQ Requirement	<b>UoM Requirement</b>			RANKING
						30 % of CLoI	50 % of CLoI			ORDER
EN ISO 11885	WW	2.4		96.7		2	2	eee	00	25
EN ISO 15586	WW	2		8		2	2	eee	00	25
ISO 17294	ង	3.8		102.5	0.01	2	2	ecc	00	25
US EPA 200.7	ш	4.75		8	2	2	2	eee	00	35
US EPA 200.8	<b>u</b>	2.5		913	0.1	2	2	eee	00	35
US EPA 6020A	Å	11.9				2	2	eec	00	65
US EPA 6010	AdW	20		107	1.2	2	2	θŒ	00	45
MEWAM 1638	S	1.7		84.7	0.27	2	2	<del>ecc</del>	00	35
						If 0, does not comply	If 0, does not comply			

If 2, no UoM requirement

If 2, no LoQ requirement

If 1, complies

If 1, complies

DW drinking water GW ground water RW river water ReW reagent water AS aqueous solution AdW acid-digested water WW waste water IE industrial effluent

SS synthetic standard

U unknown

SE sewage effluent

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