

Report

Report no.19/22

Guidance to Registrants on Methods for the Identification of Petroleum UVCB Substances for REACH



Guidance to Registrants on Methods for the Identification of Petroleum UVCB Substances for REACH

This report was prepared by S. Forbes (SF Analyticon Limited) under the supervision of C. Banner (Concawe) at the request of Concawe Substance Identity Management Group (SIMG).

Thanks to members of Concawe SIMG for their input and review.

Reproduction permitted with due acknowledgement

© Concawe
Brussels
December 2022

ABSTRACT

Following recent revisions to Annex VI of EU REACH Regulation No. 1907/2006, this report describes the information which registrants should now provide in Sections 1.2 and 1.4 of the IUCLID registration dossier for the identification of their petroleum UVCB substances.

ECHA strongly recommends the use of common analytical procedures to ensure comparability of compositional information between different registrations and this report therefore lists the specific industry standard methods recommended by Concawe for characterising petroleum UVCB substances.

KEYWORDS

REACH, Annex VI, UVCB, petroleum substance, substance identification, analytical characterisation, industry standard method, recommended analytical method, Concawe guidance, constituents, spectral information

INTERNET

This report is available as an Adobe pdf file on the Concawe website (www.concawe.org).

NOTE

Considerable efforts have been made to assure the accuracy and reliability of the information contained in this publication. However, neither Concawe nor any company participating in Concawe can accept liability for any loss, damage or injury whatsoever resulting from the use of this information.

This report does not necessarily represent the views of any company participating in Concawe.

CONTENTS		Page
1.	INTRODUCTION	1
2.	REACH ANNEX VI REQUIREMENTS	2
3.	RECOMMENDED METHODS	3
4.	REFERENCES	4
5.	ABBREVIATIONS	5
APPENDIX 1	RECOMMENDED METHODS GROUPED ACCORDING TO SUBSTANCE CATEGORY	6
APPENDIX 2	RECOMMENDED METHODS GROUPED ACCORDING TO THE TYPE OF SUBSTANCE IDENTITY INFORMATION PROVIDED	7

Disclaimer

The information contained in this report should only be regarded as guidance provided by Concawe for the benefit of registrants. Concawe cannot guarantee that following this guidance will satisfy the requirements of ECHA and it is therefore possible that additional substance identity information might be requested.

1. INTRODUCTION

EU REACH Regulation No. 1907/2006 covering the production and use of chemical substances and their potential impacts on human health and the environment came into force in 2007. Annex VI of this regulation contains information on the type of information on substance identity which registrants should provide in the dossiers which they submit to ECHA.

Since the introduction of REACH, Concawe has provided guidance ^[1,2,3,4,5] to member companies on the type of analytical information which should be generated for the identification of petroleum UVCB substances and on the methods which should be employed to generate this information. ECHA has always encouraged the use of industry standard methods for substance identification purposes to ensure comparability of compositional information between different registrations, and the Concawe guidance has therefore always recommended the use of such methods (e.g. ISO; EN; ASTM; IP). These methods have been developed and validated by the petroleum industry and therefore provide directly comparable data on substances manufactured by different registrants and analysed in different laboratories. Moreover, they are accepted by customers and competent authorities as a good technical basis for confirming product quality and assessing potential health, safety and environmental hazards associated with these materials.

Annex VI of the REACH Regulation has recently been revised ^[6] and, given the current requirements relevant to UVCB substances, this report describes the information which registrants should now provide in Sections 1.2 and 1.4 of the IUCLID registration dossier for substance identification purposes; and lists the specific industry standard methods which should be employed to generate this information.

2. REACH ANNEX VI REQUIREMENTS

Following the recent revisions of Annex VI, the key requirements for identification of petroleum UVCB substances are:

- Description of the origin or source and the manufacturing process.
- Names of constituents present at a concentration of $\geq 10\%$.
- Names of known constituents present at a concentration of $\leq 10\%$.
- For constituents that cannot be identified individually, description of groups of constituents based on chemical nature.

In this context a constituent means a discrete chemical structure which is separable from its stereo-, regio- and constitutional isomers.

A known constituent is any constituent measured using the methods described in this report but, given that all the methods cited for substances other than naphthas only provide information on groups of constituents and not discrete components, this requirement is only applicable to substances in the naphtha category and other substances with a maximum boiling point of 225 °C.

Given that the formal descriptions of most petroleum UVCB substances include information on carbon number and/or boiling range, registrants should also provide this information to substantiate the identity of the substance. Similarly for those substances where viscosity is defined in the formal descriptions, such as lubricant base oils, it is necessary to provide this information for substance identification purposes.

Spectral Information

In addition to the key requirements shown above, Annex VI now states that all necessary qualitative analytical data specific for the identification of the substance, such as UV, IR, NMR, MS or diffraction data, should also be provided by registrants. However, Concawe does not recommend the inclusion of such data because they provide no additional substance identity information to that obtained from the methods described in this report.

Concawe has provided justification ^[7] for this claim by presenting the spectral data generated by UV, IR, ¹H-NMR and ¹³C-NMR during the Concawe 2015 Analytical Program ^[8], which involved the chemical characterisation of 189 registered petroleum UVCB substances from 20 substance categories. This study showed that most substances cannot be effectively differentiated from each other using these spectroscopic techniques.

The only substances which justify the provision of any spectral data are those where the absence of aromatic or olefinic components is of critical importance, such as highly refined base oils (white mineral oils). Trace concentrations of these unsaturated compounds produce significant absorption bands in the 200-300 nm spectral region and UV data can therefore provide useful additional chemical compositional information on these substances.

For other petroleum UVCB substances Concawe recommends that registrants waive the inclusion of spectral data in their submissions based on the argument that “*such data provide no additional substance identity information to that obtained using the techniques described in the submission*” and citing the scientific justification for this waiver ^[7]. This said, Concawe cannot guarantee that following this guidance will satisfy the requirements of ECHA and some submissions without spectral data have been known to fail completeness checks.

3. RECOMMENDED METHODS

The methods recommended for substance identification are listed in Appendices 1 and 2.

Appendix 1 shows the methods relevant for each petroleum substance category. Most of these methods were developed for product specification purposes rather than to provide chemical compositional information, and it is therefore essential to check that the substances under investigation are within the scope of the method and do not contain components which are known to interfere with the measurement. In this context it is possible that a method could be used to accurately measure analyte concentrations beyond those specified in the method, but the quoted precision data would not apply in such cases.

Appendix 2 lists the same methods as those shown in Appendix 1 but grouped according to the type of substance identity information provided, such as boiling point/carbon number range or hydrocarbon class.

Non-Standard Methods

Although it is recommended that the industry standard methods shown in Appendices 1 and 2 are used for the identification of petroleum UVCB substances, it is possible to use “equivalent” methods where there is clear evidence that they yield the same results as the standard methods.

It is also possible that some samples of petroleum UVCB substances might not be amenable to analysis using the recommended methods and that modifications to a method might be required for characterising such samples (e.g. the use of ASTM D2007_19 for the analysis of wax samples as shown in Appendix 2).

Despite the recommendation to employ industry standard methods for substance identification, the provision of analytical data generated using such methods will not necessarily satisfy ECHA’s requirements, and additional compositional information might be requested. Concawe has submitted data generated using non-standard methods, such as GCxGC and FIMS, to support proposals for read-across between substances but it is recognised by ECHA ^[9] that the level of compositional information required to support read-across may be higher than that required for substance identification.

Additional Analytical Information

This report is only concerned with the provision of analytical information for substance identification purposes, and not with analytical data which might be required for other purposes such as Classification, Labelling and Packaging (CLP) regulations or Persistence, Bioaccumulation and Toxicity (PBT) assessments. For these purposes registrants are required to provide analytical information on compounds such as benzene, toluene, ethylbenzene, xylene, cumene, n-hexane, PAHs and other SVHCs if they believe them to be present in any of their petroleum UVCB substances. Concawe is planning to produce a separate report providing more detailed information on this subject.

4. REFERENCES

1. Guidance on Analytical Requirements for Petroleum UVCB Substances - Completion of REACH Registration Dossiers (Version 1.5)-Concawe - December 2010
2. Guidance on Analytical Requirements for Petroleum UVCB Substances - Completion of REACH Registration Dossiers (Version 2.0)-Concawe - May 2014
3. Substance Identification Profiles (SIP) for Petroleum Substances-Concawe - September 2017
4. Guidance to Registrants on Methods for the Characterisation of Petroleum UVCB Substances for REACH Registration Purposes -Concawe - April 2020
5. REACH - Analytical Characterisation of Petroleum UVCB Substances -Concawe Report No. 7/12 - October 2012 - [Microsoft Word - Rpt_12-7.doc \(concawe.eu\)](#)
6. EU Commission Regulation 2022/477 of 24 March 2022 amending Annexes VI to X to Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)
This regulation shall apply from 14 October 2022
7. Investigation of the value of spectral data for the identification of petroleum UVCB substances - Concawe Report No. 09/20 - June 2020 - https://www.concawe.eu/wp-content/uploads/Rpt_20-09.pdf
8. Concawe Substance Identification Group Analytical Program Report (Abridged Version) Concawe Report No. 5/19 - July 2019
<https://www.concawe.eu/wp-content/uploads/Concawe-Substance-Identification-Group-Analytical-Program-Report-Abridged-Version.pdf>
9. ECHA Advice on using read-across for UVCB substances Obligations arising from Commission Regulation 2021/979, amending REACH annexes May 2022
[advice_uvcb_read-across_en.pdf](#)

Copies of references 1 - 4 can be obtained by contacting Concawe

5. ABBREVIATIONS

REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
UVCB	Unknown or Variable Composition, Complex Reaction Products or Biological Materials
UV	Ultra-Violet
IR	Infra-Red
NMR	Nuclear Magnetic Resonance
MS	Mass Spectroscopy
SIMDIS-GC	Simulated Distillation Gas Chromatography
TBP	True Boiling Point
GCxGC	Comprehensive Two-Dimensional Gas Chromatography
FIMS	Field Ionisation Mass Spectroscopy
PAH	Polyaromatic Hydrocarbon
SVHC	Substance of Very High Concern

APPENDIX 1 RECOMMENDED METHODS GROUPED ACCORDING TO SUBSTANCE CATEGORY

The registrant is responsible for checking that the substance being analysed is within the scope of the selected method (see Appendix 2).

Substance	Applicable methods for measurement of boiling point / carbon number ranges	Applicable methods for measurement of hydrocarbon class
Naphthas	ASTM D7096_19; ASTM D5399_09	ISO 22854_21; ASTM D6839_21 ASTM D5134_13; ASTM D6729_20; ASTM D6730_21 (individual components)
Kerosines/MK1 Diesel Fuel	ISO 3924_19; ASTM D2887_19; IP 406_14; ASTM D7798_20; ASTM D7807_20	ASTM D6379_21
Gas Oils	ISO 3924_19; ASTM D2887_19; IP 406_14; EN 15199-1_20; ASTM D7500_15; ASTM D7798_20; ASTM D7807_20; ASTM D7213_15	EN 12916_19; ASTM D6591_19
Base/Foots Oils	EN 15199-1_20; EN 15199-2_20; ASTM D7500_15; ASTM D6352_19; ASTM D7213_15	IP 368_06; ASTM D7419_18; ASTM D2007_19; IP 346_92
Waxes/Petrolatums	EN 15199-1_20; EN 15199-2_20; ASTM D7500_15; ASTM D6352_19; ASTM D7213_15	ASTM D2007_19; IP 469_06
Aromatic Extracts	EN 15199-1_20; EN 15199-2_20; ASTM D7500_15; ASTM D6352_19; ASTM D7213_15	ASTM D2007_19; IP 469_06
Heavy Fuel Oils	EN 15199-2_20; ASTM D7169_20	ASTM D2007_19; IP 469_06
Bitumens/Oxidised Asphalts	EN 15199-2_20; ASTM D7169_20	ASTM D2007_19; IP 469_06

APPENDIX 2 RECOMMENDED METHODS GROUPED ACCORDING TO THE TYPE OF SUBSTANCE IDENTITY INFORMATION PROVIDED

The registrant is responsible for checking that the substance being analysed is within the scope of the selected method.

Methods for measurement of boiling point / carbon number ranges

Method	Title	Scope
ASTM D7096_19	<i>Standard Test Method for Determination of the Boiling range Distribution of Gasoline by Wide-Bore Capillary Gas Chromatography</i>	FBP <280 °C
ISO 3924_19	<i>Determination of boiling range distribution - Gas chromatography method</i>	FBP <538 °C
ASTM D2887_19	<i>Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography</i>	FBP <538 °C
IP 406_14	<i>Determination of boiling range distribution by gas chromatography</i>	FBP <538 °C
EN 15199-1_20	<i>Determination of boiling range distribution by gas chromatography method - Part 1: Middle distillates and lubricating base oils</i>	IBP >100 °C FBP <750 °C
EN 15199-2_20	<i>Determination of boiling range distribution by gas chromatography method - Part 2: Heavy distillates and residual fuels</i>	IBP >100 °C FBP >750 °C
ASTM D7169_20	<i>Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography</i>	FBP >720 °C
ASTM D7500_15	<i>Standard Test Method for Determination of Boiling Range Distribution of Distillates and Lubricating Base Oils—in Boiling Range from 100 °C to 735 °C by Gas Chromatography</i>	IBP >100 °C FBP <735 °C
ASTM D6352_19	<i>Standard Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 °C to 700 °C by Gas Chromatography</i>	IBP >174 °C FBP <700 °C

Method	Title	Scope
ASTM D7798_20	<i>Standard Test Method for Boiling Range Distribution of Petroleum Distillates with Final Boiling Points up to 538 °C by Ultra Fast Gas Chromatography (UF GC)</i>	FBP <538 °C
ASTM D5399_09	<i>Standard Test Method for Boiling Point Distribution of Hydrocarbon Solvents by Gas Chromatography</i>	IBP >37 °C FBP <285 °C
ASTM D7807_20	<i>Standard Test Method for Determination of Boiling Range Distribution of Hydrocarbon and Sulfur Components of Petroleum Distillates by Gas Chromatography and Chemiluminescence Detection</i>	FBP <538 °C
ASTM D7213_15	<i>Standard Test Method for Boiling Range Distribution of Petroleum Distillates in the Boiling Range from 100 °C to 615 °C by Gas Chromatography</i>	IBP >100 °C FBP <615 °C

Physical distillation is also an option for measuring the boiling point range of naphthas, kerosines and gas oil samples but the correlation procedures for the conversion of physical distillation data into SIMDIS-GC and TBP carbon number ranges are not truly robust. Discrepancies between physical distillation and SIMDIS-GC can be as high as 20% at each end of the boiling point range and the latter technique is the preferred procedure for generating substance identity information.

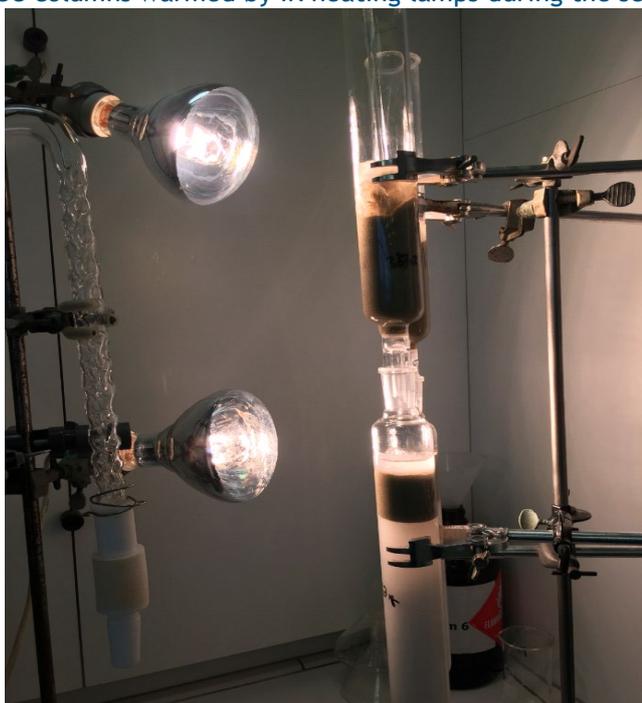
Methods for measurement of hydrocarbon class (groups of constituents)

Method	Title	Scope
ASTM D6379_21	<i>Standard Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection</i>	IBP >50 °C; FBP <300 °C <44.0% mono-aromatics <6.2% di-aromatics <50.0% total aromatics
EN 12916_19	<i>Determination of aromatic hydrocarbon types in middle distillates - High performance liquid chromatography method with refractive index detection</i>	IBP >150 °C; FBP <400 °C <30.0% mono-aromatics <10.0% di-aromatics <2.0% tri-aromatics <42.0% total aromatics
ASTM D6591_19	<i>Standard Test Method for Determination of Aromatic Hydrocarbon Types in Middle Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection</i>	IBP >150 °C; FBP <400 °C <40.0% mono-aromatics <20.0% di-aromatics <6.0% tri-aromatics <65.0% total aromatics

Method	Title	Scope
IP 368_06	<i>Determination of hydrocarbon types in lubricating oil basestocks - Preparative high performance liquid chromatography method</i>	IBP >270 °C
ASTM D7419_18	<i>Standard Test Method for Determination of Total Aromatics and Total Saturates in Lube Basestocks by High Performance Liquid Chromatography (HPLC) with Refractive Index Detection</i>	<25.0% aromatics 75.0-100.0% saturates
ASTM D2007_19 <u>see notes below</u>	<i>Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum-Derived Oils by the Clay-Gel Absorption Chromatographic Method</i>	IBP >260 °C

For some paraffin and hydrocarbon waxes, petrolatum and slack waxes, which are not easily solubilised in the pentane sample solvent specified in ASTM D2007_19, the following modifications have been employed:

- smaller sample intake (1-2 g rather than 10 g)
- sample dissolved in cyclohexane rather than n-pentane
- LCC columns warmed by IR heating lamps during the separation as shown below



IP 469_06	<i>Determination of saturated, aromatic and polar compounds in petroleum products by thin layer chromatography and flame ionisation detection</i>	IBP >300 °C
IP 346_92	<i>Determination of polycyclic aromatics in unused lubricating base oils and asphaltene free petroleum fractions - Dimethyl sulfoxide extraction refractive index method</i>	IBP >300 °C

Methods for measurement of carbon number and hydrocarbon class (groups of constituents)

Method	Title	Scope
ISO 22854_21	<i>Determination of hydrocarbon types and oxygenates in automotive motor gasoline and in ethanol (E85) automotive fuel – Multidimensional gas chromatography method</i>	<26.9% olefins <46.3% aromatics <2.0% benzene <31.7% toluene
ASTM D6839_21	<i>Standard Test Method for Hydrocarbon Types, Oxygenated Compounds, Benzene, and Toluene in Spark Ignition Engine Fuels by Multidimensional Gas Chromatography</i>	<30.0% olefins <50.0% aromatics <2.0% benzene

Methods for measurement of individual constituents

Method	Title	Scope
ASTM D5134_13	<i>Standard Test Method for Detailed Analysis of Petroleum Naphthas through n-Nonane by Capillary Gas Chromatography</i>	FBP <151° C <2.0% olefins
ASTM D6729_20	<i>Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography</i>	FBP <225° C <25.0% olefins
ASTM D6730_21	<i>Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100-Metre Capillary (with Precolumn) High- Resolution Gas Chromatography</i>	FBP <225° C <25.0% olefins

Methods for measurement of other parameters

Method	Title	Scope
ASTM D445_21; ISO 3104_20	<i>Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)</i>	0.2 - 300,000 cSt

Concawe
Boulevard du Souverain 165
B-1160 Brussels
Belgium

Tel: +32-2-566 91 60
Fax: +32-2-566 91 81
e-mail: info@concawe.org
<http://www.concawe.eu>

ISBN 978-2-87567-167-7



9 782875 671677 >