IUCLID 5 COMPOSITION AND ANALYSIS GUIDANCE DOCUMENT:

IRON [EINECS NUMBER 231-096-4, CAS NUMBER 7439-89-6] including IRON, FURNACE [EINECS NUMBER 265-998-4 CAS NUMBER 65996-67-0]

SAMENESS

For the purposes of REACH iron [EINECS No. 231-096-4] and iron, furnace [EINECS No. 265-998-4] are considered as the same substance. Iron therefore covers elemental iron, iron produced in a blast furnace or by direct reduction without melting, iron powders and carbonyl iron. The identity of iron is summarised in Table 1 and the sameness specification is listed in Table 2.

Table 1: Identity of iron

Chemical name	Iron
IUPAC name	
Other names	Iron, Furnace [pig iron, plate iron, granulated iron, hot metal, , direct reduced iron (DRI), hot briquetted iron (HBI)], iron powder, carbonyl iron
EINECS Nos.	231-096-4, 265-998-4
CAS name and CAS No.	Iron 7439-89-6
Other identity code: Related CAS No.	
Molecular formula	Fe
MW (g/mole)	55.85

Table 2: Sameness specification for iron

Chemical analysis	Value
Fe	>80%
No impurities present which would give rise to classification and labelling issues.	

The physical form of the iron will vary according to the actual product from massive to fine powder as shown in Table 3.

Table 3: Physical forms of iron

Product	**Physical form**
Iron [elemental, in steel and alloys]	Massive /powders
Iron, furnace [pig iron, plate iron, granulated iron, hot metal]	Massive
Iron, furnace [Direct reduced iron (DRI)]	Pellets or lumps
Iron, furnace [Hot briquetted iron (HBI)]	Briquettes
Iron powder	Powder
Carbonyl iron	Fine powder

ANALYSIS TECHNIQUES

Techniques used for the analysis of iron depend on the type of product undergoing analysis. For iron, furnace, iron powders and carbonyl iron only the impurity elements, such as carbon, silicon, sulphur, phosphorus, manganese, calcium, aluminium etc., are measured and the total iron content, if required, is determined by difference. For direct reduced iron products, such as DRI or HBI, which are traded on the basis of their metallic iron content, the actual iron content is normally determined directly.

Analysis of elemental Iron

By definition in REACH, the composition of elemental iron is 100% Fe. It has been strongly recommended that the registrant of ferro alloys/alloys has to register each elemental metal in a special preparation and not the ferro alloys/alloys as multi-constituent substances. It is not practicable for producers and importers of ferro alloys to prove sameness of iron as such. Instead, refer to the analysis methods used for the characterisation of your ferro-alloys. Examples of analytical standards for ferro-alloys are given in the list below.

- CEN/TR 10261:2008 Iron and steel - Review of available methods of chemical analysis
- CEN/TR 10317:2009 European certified reference materials (EURONORM-CRMs) for the determination of the chemical composition of iron and steel products prepared under the auspices of the European Committee for Iron and Steel Standardization
- CEN/TR 10345:2008 Guideline for statistical data treatment of inter laboratory tests for validation of analytical methods
- CEN/TR 10350:2009 Analysis of steels and irons - Internal laboratory procedure for checking the accuracy of an analytical method by using Certified Reference Materials
- CR 10299:1998 Guidelines for the preparation of standard routine methods with wavelength-dispersive X-ray fluorescence spectrometry
- CR 10316:2001 Optical emission analysis of low alloy steels (routine method) - Guidelines for the preparation of standard routine method for optical emission spectrometry
- CR 10320:2004 Optical emission analysis of low alloy steels (routine method) - Method for determination of C, Si, S, P, Mn, Cr, Ni and Cu
- CR 10321:2003 Chemical analysis of ferrous materials - Recommendations for the drafting of standard methods of analysis employing flame atomic absorption spectrometry for the chemical analysis of iron and steel
- CR 10322:2003 Chemical analysis of ferrous materials - Operational guidelines for the application of flame atomic absorption spectrometry in standard methods for the chemical analysis of iron and steel
- EN 10036:1991 Chemical analysis of ferrous materials - Determination of total carbon in steels and irons - Gravimetric method after combustion in a stream of oxygen
- EN 10071:1991 Chemical analysis of ferrous materials - Determination of manganese in steels and irons - Electrometric titration method
- EN 10136:1991 Chemical analysis of ferrous materials - Determination of nickel in steels and irons - Flame atomic absorption spectrometric method
- EN 10177:1989 Chemical analysis of ferrous materials - Determination of calcium in steels - Flame atomic absorption spectrometric method
- EN 10178:1989 Chemical analysis of ferrous materials - Determination of niobium in steels - Spectrophotometric method

- EN 10179:1989 Chemical analysis of ferrous materials - Determination of nitrogen (trace mounts) in steel - Spectrophotometric method
- EN 10181:1989 Chemical analysis of ferrous materials - Determination of lead in steels - Flame atomic absorption spectrometric method
- EN 10184:2006 Chemical analysis of ferrous materials - Determination of phosphorus in non-alloyed steels and irons - Molybdenum blue spectrophotometric method
- EN 10188:1989 Chemical analysis of ferrous materials - Determination of chromium in steels and irons - Flame atomic absorption spectrometric method
- EN 10200:1992 Chemical analysis of ferrous materials. Determination of boron in steel. Spectrophotometric method
- EN 10211:1996 Chemical analysis of ferrous materials - Determination of titanium in steel and iron - Flame atomic absorption spectrometric method
- EN 10212:1996 Chemical analysis of ferrous materials - Determination of arsenic in steel and iron - Spectrophotometric method
- EN 10276-1:2000 Chemical analysis of ferrous materials - Determination of oxygen in steel and iron - Part 1: Sampling and preparation of steel samples for oxygen determination
- EN 10276-2:2003 Chemical analysis of ferrous materials - Determination of oxygen content in steel and iron - Part 2: Infrared method after fusion under inert gas
- EN 10315:2006 Routine method for analysis of high alloy steel by X-ray Fluorescence Spectrometry (XRF) by using a near by technique
- EN 10318:2005 Determination of thickness and chemical composition of zinc- and aluminium-based metallic coatings Routine method
- EN 24159:1989 Ferromanganese and ferrosilicomanganese - Determination of manganese content - Potentiometric method (ISO 4159:1978, ed. 1)
- EN 24159:1989/AC1:1989 Ferromanganese and ferrosilicomanganese - Determination of manganese content - Potentiometric method (ISO 4159:1978, ed. 1)
- EN 24829-1:1990/AC:1991 Steel and cast iron - Determination of total silicon content - Reduced molybdosilicate spectrophotometric method - Part 1: Silicon content between 0,05 and 1% (ISO 4829-1:1986)
- EN 24829-2:1990/AC:1991 Steel and cast iron - Determination of total silicon content - Reduced molybdosilicate spectrophotometric method - Part 2: Silicon content between 0,01 and 0,05% (ISO 4829-2:1988)
- EN 24935:1991 Steel and iron - Determination of sulphur content - Infrared absorption method after combustion in an induction furnace (ISO 4935:1989)
- EN 24937:1990/AC:1991 Steel and iron - Determination of chromium content - Potentiometric or visual method (ISO 4937:1986)
- EN 24938:1990/AC:1991 Steel and iron - Determination of nickel content - Gravimetric or titrimetric method (ISO 4938:1988)
- EN 24943:1990/AC:1991 Steel and cast iron - Determination of copper content - Flame atomic absorption spectrometric method (ISO 4943:1985)
- EN 24946:1990/AC:1991 Steel and cast iron - Determination of copper content - 2,2'diquinolyl spectrophotometric method (ISO 4946:1984)
- EN 24947:1991 Steel and cast iron - Determination of vanadium content - Potentiometric titration method (ISO 4947:1986)

- EN 29658:1991 Steel - Determination of aluminium content - Flame atomic absorption spectrometric method (ISO 9658:1990)
- EN ISO 10280:1995 Steel and iron - Determination of titanium content - Diantipyrylmethane spectrophotometric method (ISO 10280:1991)
- EN ISO 10700:1995 Steel and iron - Determination of manganese content - Flame atomic spectrometric method (ISO 10700:1994)
- EN ISO 10714:2002 Steel and iron - Determination of phophorus content - Phosphovanadomolybdate spectrophotometric method (ISO 10714:1992)
- EN ISO 10720:2007 Steel and iron - Determination of nitrogen content - Thermal conductimetric method after fusion in a current of inert gas (ISO 10720:1997)
- EN ISO 13900:2002 Steel - Determination of boron content - Curcumin spectrophotometric method after distillation (ISO 13900:1997)
- EN ISO 14284:2002 Steel and iron - Sampling and preparation of samples for the determination of chemical composition (ISO 14284:1996)
- EN ISO 15349-2:2003 Unalloyed steel - Determination of low carbon content - Part 2: Infrared absorption method after combustion in an induction furnace (with preheating) (ISO 15349-2:1999)
- EN ISO 4934:2003 Steel and iron - Determination of sulfur content - Gravimetric method (ISO 4934:2003)
- EN ISO 4945:2009 Steel - Determination of nitrogen content - Spectrophotometric method (ISO 4945:1977)
- EN ISO 9556:2001 Steel and iron - Determination of total carbon content - Infrared absorption method after combustion in an induction furnace (ISO 9556:1989)
- EN ISO 15350:2010 Steel and iron - Determination of total carbon and sulfur content - Infrared absorption method after combustion in an induction furnace (routine method) (ISO 15350:2000)
- EN ISO 15351:2010 Steel and iron - Determination of nitrogen content - Thermal conductimetric method after fusion in a current of inert gas (Routine method) (ISO 15351:1999)
- EN ISO 439:2010 Steel and iron - Determination of total silicon content - Gravimetric method (ISO 439:1994)

Analysis of Iron, Furnace [pig iron, plate iron, granulated iron, hot metal]

Iron furnace is a massive material and thus, the dry analytical techniques are recommended. There is no modification of the matrix to the sampling preparations (grinding…).

Multi-element analysis may be performed on rapidly chilled samples with a white iron structure [no graphitic carbon present in the structure] by direct reading spark source optical emission spectrometry. Alternatively, carbon and sulphur may be determined by gravimetric analysis or by infra-red absorption after combustion of the sample in oxygen. Other elements, such as aluminium, manganese, calcium, phosphorus, silicon etc., may be determined by wet chemical procedures involving gravimetric, spectro-photometric, atomic-absorption spectrometry or inductively coupled plasma atomic emission or inductively coupled plasma mass spectrometry techniques. Appropriate standard methods for the analysis of iron furnace are listed in Table 4.

Table 4: Standard methods applicable for the analysis of iron furnace

Element	Standard	Standard title and method
Carbon (<6.0 %)	ISO 437:1982	Steel and cast iron -- Determination of total carbon content -- Combustion gravimetric method

Element	Standard	Standard title and method
	ISO/TR 4830-4:1978	Steel -- Determination of low carbon contents -- Part 4: Coulometric method after combustion
	ISO 9556:1989	Steel and iron -- Determination of total carbon content -- Infrared absorption method after combustion in an induction furnace
	ISO 15350:2010	Steel and iron -- Determination of total carbon and sulphur content -- Infrared absorption method after combustion in an induction furnace (routine method)
	ISO/TR 10719:1994	Steel and iron -- Determination of non-combined carbon content -- Infrared absorption method after combustion in an induction furnace
	ASTM E1019 - 08	Standard Test Methods for Determination of Carbon, Sulphur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Fusion Techniques
Silicon (<5.0 %)	ISO 439:2010	Steel and iron -- Determination of total silicon content -- Gravimetric method
	ISO 4829-1:1986	Steel and cast iron -- Determination of total silicon content -- Reduced molybdosilicate spectrophotometric method -- Part 1: Silicon contents between 0.05 and 1.0 %
	ISO 4829-2:1988	Steel and iron -- Determination of total silicon content -- Reduced molybdosilicate spectrophotometric method -- Part 2: Silicon contents between 0.01 and 0.05 %
Aluminium	ISO 9658:1990	Steel -- Determination of aluminium content -- Flame atomic absorption spectrometric method
Calcium, Magnesium	ISO/AWI 13933	Steel and iron -- Determination of calcium and magnesium -- Inductively coupled plasma atomic emission spectrometric method
Phosphorus (<2.0 %)	ISO 10714:1992	Steel and iron -- Determination of phosphorus content -- Phosphovanadomolybdate spectrophotometric method
Sulphur (<0.4 %)	ISO 15350:2010	Steel and iron -- Determination of total carbon and sulphur content -- Infrared absorption method after combustion in an induction furnace (routine method)
	ISO 13902:1997	Steel and iron -- Determination of high sulphur content -- Infrared absorption method after combustion in an induction furnace
	ISO 10701:1994	Steel and iron -- Determination of sulphur content -- Methylene blue spectrophotometric method
	ISO 4934:2003	Steel and iron -- Determination of sulphur content -- Gravimetric method
	ISO 4935:1989	Steel and iron -- Determination of sulphur content -- Infrared absorption method after combustion in an induction furnace
	ASTM E1019 - 08	Standard Test Methods for Determination of Carbon, Sulphur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Fusion Techniques
Oxygen	ISO 17053:2005	Steel and iron -- Determination of oxygen -- Infrared method after fusion under inert gas
	ASTM E1019 - 08	Standard Test Methods for Determination of Carbon, Sulphur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Fusion Techniques
	SS-EN 10276-2	Chemical analysis of ferrous materials. Determination of oxygen in steel and iron. Infrared method after fusion under inert gas
Nitrogen	ISO 15351:2010	Steel and iron -- Determination of nitrogen content -- Thermal conductimetric method after fusion in a current of inert gas (Routine method)
	ISO 10720:1997	Steel and iron -- Determination of nitrogen content -- Thermal conductimetric method after fusion in a current of inert gas

Element	Standard	Standard title and method
	ISO 10702:1993	Steel and iron -- Determination of nitrogen content -- Thermal conductimetric method after fusion in a current of inert gas
Multi-elements analysis	ASTM E 1999-99 (2004)	Standard test method for analysis of cast iron using optical emission spectrometry

To demonstrate compliance with the sameness criteria the total iron content is determined by difference by subtracting the concentrations of the other constituents from 100%. However, if required it is possible to determine the iron content directly by wet chemistry methods, although this is not conventionally carried out in the analysis of iron furnace.

Analysis of Iron, furnace [DRI and HBI]

Table 5: Standard methods applicable for the analysis of direct reduced iron

Element	Standard	Standard title and method
Carbon and sulphur	ISO 9686:2006	Direct reduced iron. Determination of carbon and/or sulphur. High-frequency combustion method with infrared measurement.
Metallic iron	**ISO/DTS 16878** **ISO 5416:2006**	**Direct reduced iron and hot briquetted iron. Determination of metallic iron content -- Iron (III) chloride titrimetric method** **Direct reduced iron. Determination of metallic iron. Bromine-methanol titrimetric method.**
Aluminium, calcium, phosphorus, magnesium, manganese, silicon and titanium.	ISO 11535:2006	Iron ores. Determination of various elements. Inductively coupled plasma atomic emission spectrometric method.

For direct reduced forms of iron determination of the metallic iron (elemental iron) content is required. The analysis is performed by wet chemistry methods after dissolution of the metallic iron in a mixture of bromine and methanol. The carbon and sulphur contents of DRI or HBI are determined by infrared absorption after fusion of a sample of the material in an oxygen atmosphere, while other elements associated with the non-metallic fraction (gangue) may be determined by an inductively coupled plasma spectrometric or by X-Ray fluorescence methods. Examples of applicable methods are listed in Table 5.

The bromine methanol method is not advised to be used on a regular basis due to human health risks.

Analysis of iron powders and carbonyl iron

For high purity products such as iron powders and carbonyl iron it is also normal only to analyse the iron for trace impurities, such as carbon, sulphur, manganese, copper, nickel, chromium, molybdenum, vanadium, oxygen and nitrogen. It is not normal practice to analyse the iron powders for total iron content, but particle size analysis may be carried out. Examples of standard methods that may be applied are given in Table 6.

Table 6: Standard methods applicable for the analysis of iron powders

Element	Standard	Standard title and method
Carbon and sulphur	ISO 15350:2010	Steel and iron -- Determination of total carbon and sulphur content -- Infrared absorption method after combustion in an induction furnace (routine method)
	ASTM E1019-08	Standard test methods for determination of carbon, sulphur, nitrogen and oxygen in steel, iron, nickel and cobalt alloys by various combustion and fusion techniques.
Oxygen	EN 10276-2	Chemical analysis of ferrous metals. Determination of oxygen in steel and iron. Infrared method after fusion in inert gas.
	ASTM E1019-08	Standard test methods for determination of carbon, sulphur, nitrogen and oxygen in steel, iron, nickel and cobalt alloys by various combustion and fusion techniques.
Nitrogen	ISO 15351:2010	Steel and iron. Determination of nitrogen content. Thermal conductimetric method after fusion in a current of inert gas. (Routine method)
	ASTM E1019-08	Standard test methods for determination of carbon, sulphur, nitrogen and oxygen in steel, iron, nickel and cobalt alloys by various combustion and fusion techniques.
Manganese, nickel, chromium, molybdenum, copper and vanadium	ASTM E322-96	Standard test method for X-ray emission spectrometric analysis of low-alloy steels and cast irons.
Copper, nickel and molybdenum	ASTM E572-02a	Standard test method for analysis of stainless and alloy steels by X-ray fluorescence spectrometry.
Particle size analysis	ISO 4497:1983	Metallic powders. Determination of particle size by dry sieving.

To demonstrate compliance with the sameness criteria, the total iron content is determined by difference by subtracting the concentrations of the other constituents from 100%. However, if required it is possible to determine the iron content directly by wet chemistry methods, although this is generally not carried out in the analysis of iron powders.

Other techniques

Since iron is an inorganic material, analytical techniques such as nuclear magnetic resonance [NMR] spectroscopy, infra-red spectrometry [IR] and ultra-violet absorption spectro-photometry [UV] are not suitable, since these techniques are used to investigate the molecular bonding states of organic compounds that contain essentially covalent bonds. They are not appropriate methods for the identification of inorganic structures where the bonds are principally ionic or metallic in character.

Gas chromatography [GC] is also an inappropriate analytical technique for inorganic solids since it can only be applied to organic [covalent] substances that are vaporised at temperatures below ~320°C. Similarly, high-performance liquid chromatography [HPLC], which is applicable principally to organic compounds, is not a suitable method for identification of inorganic substances. Mass spectrometry can only be applied if high energy excitation techniques, such as spark discharge or laser ablation, are used to vaporise the sample for introduction into the mass spectrometer. However, these techniques essentially provide the same information as X-Ray Fluorescence [XRF] spectrometry or spark source optical emission spectrometry, which are highly developed and widely

applied for product and process control purposes. Thermo-chemical methods of analysis, such differential thermal analysis [DTA], differential scanning calorimetry [DSC] or thermo-gravimetric analysis [TGA] may be applied for specific investigations on chemical or physical phase changes and chemical reactions that occur when iron materials are heated, but the data provided by these techniques are not generally sufficient for identification of these materials.

ICP-AES [inductively coupled plasma - atomic emission spectrometry, ICP-MS [inductively coupled plasma-mass spectrometry] or AAS [atomic absorption spectrometry] methods may be used for the analysis of iron, but these techniques are generally more time-consuming and laborious than XRF spectrometry or spark source optical emission spectrometry. Moessbauer spectroscopy is a useful technique for the identification and quantification of iron-bearing phases [Fe, FeO, Fe_3O_4, Fe_2O_3, Fe_3C, calcium ferrites, $FeSiO_4$ etc.] in iron products, however, the technique is not commonly applied in industry since the instrumentation required is specialised and generally only available in research institutions. The technique is less useful than XRD since it does not provide information on non-ferrous phases such as silicates and aluminosilicates, which may be present in direct reduced iron products.

SPECTRAL IDENTIFICATION OF IRON

There are various spectral techniques that could be used for the identification of the different oxidation states of iron (Fe (0), Fe(II), Fe(III)). These include:

- X-ray diffraction analysis [XRD]
- Scanning electron microscopy coupled with energy-dispersive X-ray spectrometry
- Moessbauer spectrometry
- Spark-source mass spectrometry
- Laser ablation inductively coupled plasma mass spectrometry
- Inductively coupled plasma atomic emission spectrometry

The cited techniques are applicable to all forms of iron. However all these techniques require materials to be prepared under the powder form. This preparation of sample may influence the characteristics of the material [e.g. surface oxidation] and thus the final analytical result. However, while these techniques may provide structural information concerning the iron substance, they are unlikely to yield information useful for the determination of the sameness of the substance.