REPORT

A2.2.1: Current documentary standards or technical specifications for quality assurance hydrogen (for heat), biomethane and carbon dioxide for CCUS

Project 10IND20 "Decarbonising the gas grid"

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Summary

This report was written as part of activity A2.1.1 from the EMPIR Metrology for decarbonizing the gas grid (Decarb) project. The three-year European project started 1st June 2021 This project is the first large scale project of its kind that will tackle four measurement challenges that the gas industry needs to solve before they can decarbonise the gas grid through introduction of biomethane, hydrogen-enriched natural gas, 100 % hydrogen, and carbon capture and storage (CCS). The project covers the priority challenges within flow metering, gas composition, physical properties and safety (including monitoring of gas leaks).

In the report, we have reviewed current documentary standards or technical specifications for quality assurance hydrogen (for heat), biomethane and carbon dioxide for CCUS. Quality specifications are usually designed to minimize risks associated with the utilization, storage and/or transport of the gas and include considerations regarding the possible effect of impurities on proper and safe functioning of appliances, on the integrity of the supply pipework, on health and on the properties of the products.

Specifications for biomethane exist since 2016 (EN16723-1 and EN16723-2). However, these standards will be revised in a near future. So far, the test methods proposed in these standards are mostly offline methods developed for other matrices such as natural gas and air. These methods need to be validated properly for biomethane and possibly, new methods specifically for biomethane should be developed.

Specifications for hydrogen for heat applications are needed. The work is ongoing with a new work item proposal entitled Quality of gas – Hydrogen used in converted/rededicated gas systems being under development.

For carbon dioxide for CCS, currently, no universally agreed upon specification for CO_2 quality exists yet. Therefore, there are currently no proposed test methods. Analytical methods need to be developed for the impurities most commonly mentioned in projects that have studied CO_2 composition for CCS applications and impact of impurities and should preferably target the lowest threshold given in these documents/reports. A number of specifications already exist for different CO_2 utilizations. For most of the parameters, the most stringent limits are set in standards from EN936 and EIGA70/17 (intended for human consumption).

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1 INTRODUCTION

Hydrogen and biomethane share the same applications than natural gas, including heat applications, as vehicles fuels and for the production of electricity. They have the potential to contribute to the decarbonization of the gas grid. Carbon capture and storage (CCS) and carbon capture and utilization (CCU) may offer a response to the global challenge of significantly reducing greenhouse gas emissions. Due to the methods of production, these gases usually contain trace components that can negatively affect both the appliances they come in contact with, and the pipelines when injected in the gas grid. Therefore, a proper (and stable) gas quality which meet the requirements set in relevant standards must be guaranteed. In this study, we reviewed the current documentary standards or technical specifications for quality assurance for hydrogen (for heat), biomethane and carbon dioxide.

In Europe, the two principal sources for standards are the International Organization for Standardization (ISO) and the European Committee for standardization (CEN) where standards are produced by technical committees. However, even associations (such as European Industrial Gases Association, EIGA) produce technical reports or documents including purity specifications for different applications. Specifications has also been drawn as part of research projects. Quality specifications are usually designed to minimize risks associated with the utilization, storage and/or transport of the gas and include considerations regarding the proper and safe functioning of appliances and integrity of the supply pipework avoiding hampering supply with too restrictive limitations which would result in increased costs.

A list of committees, organizations and associations producing documentary standards was established in the project Hy4heat [1], it also included a list of relevant standards for hydrogen quality assurance and some standards relevant for natural gas and biomethane. This list was used as a starting point in this work and has been completed through a literature survey. Moreover, relevant quality specifications for carbon dioxide capture and utilization have been gathered. The main identified documentary standards or documents for gas quality specifications for these three gases; biomethane, hydrogen (for heat) and carbon dioxide are listed in Table 1.

Table 1 – Identified documentary standards or documents for gas quality specifications from different sources

Sources	Hydrogen		Biomethane		Carbon dioxide	
	Technical committees	Standards	Technical committees	Standards	Technical committees	Standards
International Organization for standardization (ISO)	ISO TC 197 Hydrogen technologies	ISO14687:2019 [2](grade B) (ISO21087)	ISO TC 193 Natural gas	48 standards for natural gas (SC1 – analysis of natural gas), some mentioning biomethane Mostly test methods	ISO TC 265 Carbon dioxide capture, transportation and geological storage	ISO TR 27921:2020 [3] ISO TR 27913:2016 [4] ISO TR 27915:2017 [5]
European committee for standardization (CEN)	CEN TC 268 Cryogenic vessels and specific hydrogen technologies applications CEN TC 234 Gas infrastructure	EN17124:2018 [6] (road application) NWIP Quality of gas – Hydrogen used in converted/rededicated gas systems [7]	CEN TC 408 Natural gas and biomethane for use in transport and biomethane for injection in the natural gas grid	EN16723-1:2016 [8] EN16723-2:2017 [9] CEN/TR 17238 [10]	CEN TC 164 water supply	EN936:2013 [11] (human consumption)
National standardization body		BIS PAS 4444:2020 [12]				
European industrial gases association (EIGA)			-			Doc. 70/17 2016 [13] (food and beverages)
Marcogaz				WG_GQ-187 [14] (technical specifications		

				for EU countries) Updated 2019		
ISBT International society of beverage technologists					Beverage gases	BVG-00001 [15] (beverages)
European Benchmarkning Task Force (2011)						Limit for CCS in aquifers and oil reservoirs (EOR) [16]
Compressed Gas Association						CGA G-6.2 – 2011 [17]
European commission						Commission Regulation (EU) No 231/2012 food additives, Annex E290, CO2 [18]

2 BIOMETHANE

For biomethane, the most widespread quality specifications are the ones set in two standards prepared by the Technical Committee CEN/TC 408 "Natural gas and biomethane for use in transport and biomethane for injection in the natural gas grid"; EN16723-1:2016 Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network – Part 1: Specifications for biomethane for injection in the natural gas network [8] and EN16723-2:2017 Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network – Part 2: Automotive fuels specification [9].

Moreover, Marcogaz (Technical Association of the European Natural Gas Industry) has regrouped in the document WG_GQ-187 [14], the quality required by legislation in some European countries (France, the Netherlands, Spain, Sweden, Germany, Schweiz, Austria, Italy, Denmark, England, Belgium and the Czech Republic) for biomethane injection into the natural gas network (last updated 2019). Besides the parameters listed in EN16723, some countries added additional ones such as limit values for mercury, chlorine, fluorine, cyanides, BTEX (Benzene, Toluene, Ethylbenzene, Xylenes), carbon dioxide and propane.

The standard EN16723-1 sets the common requirements and test methods (Table 2) for biomethane injection in the natural gas network (at the point of entry in H gas and L gas networks). The test methods are informative.

Table 2 – Common requirements and test methods for biomethane at the point of entry into H gas and L gas networks

Parameter	Unit	Max limit values	Test methods
Total volatile silicon (as Si)	mgSi/m^3	0.3 to 1*	EN ISO 16017-1 : 2000 [19]
Compressor oil			ISO8573-2 :2007 [20]
Dust impurities			ISO8573-4 :2001 [21]
Chlorinated compounds			EN1911 :2010 [22]
Fluorinated compounds			NF X43-304 :2007 [23] ISO15713 :2006 [24]
Carbon monoxide	%mol	0.1	EN ISO 6974-series [25]
Ammonia	mg/m^3	10	NEN 2826 :1999 [26] VDI3496Blatt1 :1982-04 [27] NF X43-303 :2011 [28]
Amine	mg/m^3	10	VDI2467 Blatt 2 : 1991-08 [29]

*to be agreed between biomethane producer and grid operator

Four parameters have maximal limit values: total volatile silicon, carbon monoxide, ammonia and amine. For each of these parameters, at least one test method is proposed in EN16723-1. For total volatile silicon (as Si), the method proposed - EN ISO16017:2000 [19], is based on thermal desorption and gas chromatography (with flame ionization detector, photoionization detector, mass spectrometric or other suitable detector) after active sampling on sorbent tubes. The method is intended to quantify individual compounds in air matrix.

For carbon monoxide, the method proposed, EN ISO 6974 series [25] is based on gas chromatography and is intended for natural gas matrix. For ammonia, all the methods proposed here are for sources emissions (air matrix). For amine, the method proposed here is intended for air and is based on liquid chromatography (HPLC).

Compressor oil and dust impurities have no maximal values; it is instead stated that the biomethane shall be free from impurities other than amount that does not render the biomethane unacceptable for conveyance and use in end-user applications. However, some methods are proposed for these parameters. These standards, ISO8573-2:2007 [20] and ISO8573-4:2001 [21] are intended for compressed air and include both the sampling and the analytical procedures. The oil is either collected on coalescing filters followed by weight measurement or on microfiber membrane followed by infra-red or gas chromatography (with flame ionization detector) analysis. Particles are measured using different methods such as laser particle counter, condensation nucleus counter, differential mobility scanning mobility particle sizer or microscope, after sampling on membrane depending on their sizes.

For chlorinated and fluorinated compounds, the standard EN16723-1:2016 [8] refers to a technical report prepared by CEN/TC 408, CEN/TR 17238:2018 [10] explaining an approach for the assessment of limit values for contaminants that may be found in biomethane to mitigate the potential impact on human health.

The standard EN16723-2:2017 [9] sets the requirements and test methods (Table 3) for natural gas and biomethane as automotive fuels.

Table 3: *Requirements and test methods for biomethane and natural gas as automotive fuels*

Parameter	Unit	Max limit values	Test methods
Total volatile silicon (as Si)	mgSi/m^3	Max: 0.3*	EN ISO 16017-1 : 2000 [19]
Hydrogen	%mol/mol	Max : 2	EN ISO 6974 series [25]
Hydrocarbon dew point temperature	ºC	Max : -2	ISO 23874 [30] ISO/TR 11150 [31] ISO/TR 12148 [32]
Oxygen	%mol/mol	Max : 1	EN ISO 6974 series [25] EN ISO 6975 [33]
Hydrogen sulfide + carbonyl sulfide	mg S/m^3	Max : 5	EN ISO6326-1 [34] EN ISO 6326-3 [35] EN ISO19739 [36]
S total including odorization	mg S/m^3	Max : 30	EN ISO 6326-5 [37] EN ISO19739 [36]
Methane number	Index	Min 65	Annex A of EN16726 [38]
Compressor oil	mg/m^3	Max :10	ISO8573-2 :2007 [20]
Dust impurities			ISO8573-4 :2001 [21]
Amine	mg/m^3	10	VDI 2467 Blatt 2 :1991-08 [29]
Water dew point at 20 MPa	ºC	Class A: -10 Class B: -20 Class C: -30	ISO6327 [39]

Some of these parameters and test methods are common with those from ISO16723-1:2016 [8] (silicon, compressor oil, dust, amine). Additionally, oxygen, hydrogen and sulfur compounds have requirements in term of maximal limit values that are not present in ISO16723-1:2016 [8]. Compared to ISO16723-1:2016 these specifications also contain some physical parameters, such as methane number, hydrocarbon dew point temperature and water dew point.

For oxygen and hydrogen, the test method proposed (ISO6974 series [25]) is the same method proposed for carbon monoxide in ISO16723-1:2016 [8] (based on gas chromatography and intended for natural gas matrix) with the addition of ISO6975 [33] for oxygen (gas chromatography with thermal Conductivity Detector).
For sulfur compounds, the test methods proposed are intended for natural gas and are based on Wickbold combustion method (ISO4260 [40]) or Lingener combustion method (ISO6326-5 [37]) for total sulfur and gas chromatography (ISO19739 [36]) or potentiometry (ISO6326-3 [35]) for individual sulfur compounds (such as hydrogen sulfide, H_2S or carbonyl sulfide, COS) or specific groups of sulfur compounds (e.g. thiol sulfur). Standard ISO6326-1 [34] gives a comparison of standardized methods and provides information for the choice of the method.
The water dew point is proposedly (ISO6327 [39]) determined with a hygrometer by detecting water vapour condensation occurring on a cooled surface or by checking the stability of the condensation on this surface.
For the hydrocarbon dew point temperature, the methods proposed require the knowledge of the composition (obtained by chromatography) in order to calculate the parameter using an appropriate equation of state (ISO23874 [30]) or the use of chilled mirror type instruments (ISO/TR12148:2009 [32]).
For the methane number, the method proposed (Annex A of ISO16726 [38]) is based on a calculation that requires the knowledge of the composition.
As mentioned above, most of the proposed test methods were developed for other matrices than biomethane, such as air (for a majority of the tests methods) or natural gas (which besides methane, also contains ethane, propane and other alkanes but does not contain some of the impurities that can be found in biomethane, such as terpenes, siloxanes, ketones etc. It is important to demonstrate that these methods are not matrix dependent.

A number of test methods have been developed specifically for biomethane during the EMRP project ENG54 Metrology for biogas and the EMPIR project Metrology for biomethane.

- Determination of amine content with Gas Chromatography with Flame Ionization and/or Mass Spectrometry detectors (TD-GC-MS/FID)
- Determination of ammonia with diode laser, tuneable diode laser absorption spectroscopy, cavity enhanced absorption spectroscopy or ultraviolet visible spectroscopy
- Determination of the oil content with Gas Chromatography with mass spectrometry using a specially developed sampler.
- Determination of the halogenated VOC content with TD-GC-MS/FID
- Determination of HCl and HF by ion chromatography
- Determination of siloxane content by gas chromatography ion mobility spectrometry
- Determination of the total silicon content with ICP/MWP (Inductively Coupled Plasma)/(Microwave plasma)
- Determination of siloxane content with TD-GC-MS/FID

Some of these test methods have been submitted as New Work Item Proposal to the working group WG25 of ISO/TC 193 to replace (or complement) the currently cited methods in EN16723 series.

A revision of EN16723 standards is planned in a near future.

3 HYDROGEN FOR HEAT

Hydrogen can be used as an alternative to natural gas for space heating, water heating, and for gas cooking. Hydrogen could be used to power fuel cell micro-combined Heat Power (CHP), direct flame combustion boilers, catalytic boilers and gas-powered heat pumps. All these appliances require a certain purity in order to function properly. Several other factors determine the compatibility of appliances with different types of gases, with the simplest and most commonly used comparison metric being the Wobbe index [35]. Moreover, widespread consumption of hydrogen for heating would likely require scaling up and expanding existing hydrogen networks or constructing new ones. Therefore, specifications need to consider all these aspects (the proper and safe functioning of appliances such as fuel cells, the integrity of the pipeline, etc.). As explained in WP2 Hy4heat [1], the key existing documentary standard providing requirement for hydrogen quality for heat applications is ISO14687:2019 [2] (Table 4) which includes different grades such as Grade A (residential/commercial combustion appliances e.g. boilers, cookers and similar applications) and Grade E (PEM fuel cells for stationary appliances). However, the report from Hy4Heat project which also includes discussions with stakeholders concludes that new hydrogen purity specifications for use in domestic and commercial heating applications are needed.

Table 4 – Quality specifications in ISO14687:2019 for application other than PEM fuel cell road vehicle and stationary applications

	Grade A	Grade E**	Test methods
Hydrogen fuel index (minimum mole fraction, %)	98.0%	99.9%	Calculated by subtracting the ”total non-hydrogen gases”
Total non-hydrogen gases	2%	0.1 %	Should be carried out based on the hydrogen production method
Water (mole fraction, %)	Non-condensing at all ambient conditions	Non-condensing at all ambient conditions	JIS K0512 [41] ASTM D7941 [42] Murugan and Brown [43] NPL Report AS 64 [44] ASTM D7653 [45] ASTM D7649 [46]
Total hydrocarbon	100 µmol/mol	2 µmol/mol***	ASTM D7675 [47] JIS B7956 [48] ASTM WK34574 [49][44] ASTM D7653 [45] NPL Report AS 64 [44]
Methane	-	100 µmol/mol	-
Oxygen	-	50 µmol/mol	ASTM D7607 [50] ASTM D7649 [46] ASTM D7941 [42] NPL Report AS 64 [44]
Combined oxygen, argon, nitrogen	1.9%	0.1%	ASTM D7941 [42] NPL Report AS 64 [44]
Carbon monoxide	1 µmol/mol	-	JIS K0114 [51] ASTM D7653 [45] ASTM D7941 [42] NPL Report AS 64 [44]
Sulfur	2 µmol/mol	-	ASTM D7652 [52] JIS K 0512 [41]

			Murugan and Brown [43]
Permanent particulates	*	-	

*the hydrogen shall not contain dust, sand, dirt, gums, oils and other substances in an amount sufficient to damage the fueling station equipment
**Type I, grade E, category 3 (gaseous hydrogen; high power/high efficiency applications)
***Except methane

For test methods, ISO14687:2019 [2] refers to ISO21087:2019 [53] where a list of analytical techniques suitable for measurement of impurities in hydrogen is given. The list is based on requirements for the grade D (PEM fuel cell road vehicle application) which has more stringent limits than grades A or E. These methods are either described in standards, mainly from ASTM or JIS or in technical reports such as NPL report AS 64 [44]. Several articles or documents have also compiled possible analytical methods for impurities in hydrogen, with new methods developed for example during research projects being added. Examples of these articles are Murugan and Brown [43] dated from 2015 and Beurey *et al.* [54] dated from 2021. Here also, the methods reviewed were designed to meet the stringent requirements for the grade D.

For water, the following methods are mentioned: Chilled mirror hygrometer (JIS K0512 [41]), quartz crystal microbalance, CRDS and continuous wave CRDS (ASTM D7941 [42]), capacitance (JIS K0512 [41]), GC-MS with (ASTM D7649 [42]) or without jet pulse injection, FTIR (ASTM D7653 [45], JIS K0512 [41]).
For total hydrocarbon content (THC), the following methods are mentioned: GC/FID (ASTM D7675 [47], JIS B 7956 [48]), methaniser GC-FID, GC-MS (with pre-concentrator, ASTM WK34574 [49]) and FTIR (ASTM D7653 [45]).
For oxygen, the following methods are mentioned: electrochemical sensor (ASTM D7607 [50]), GC-MS with jet pulse injection (ASTM D7649 [46], also for N_2 and Ar), GC-TCD and GC-PDHID (NPL Report AS64 [44], also for N_2 and Ar), continuous wave CRDS (ASTM D7941 [42]).
For carbon monoxide, the following methods are mentioned: GC-PDHID (NPL Report AS 64 [44]) and Methaniser-GC-FID (NPL Report AS 64 [44], JIS K 0114 [51]), FTIR (ASTM D7653 [45]), continuous wave CRDS (ASTM D7941 [42]).
For sulphur compounds, the following methods are mentioned: GC-SCD with (ASTM D7652 [52]) or without pre-concentrator (Murugan and Brown [43]), GC-FPD with pre-concentrator (JIS K 0512 [41]).

New analytical methods were developed (and validated) during the EMPIR projects “Metrology for sustainable hydrogen energy applications, 15NRM03 and Metrology for Hydrogen vehicles 1, 16ENG01. The MetroHyVe report on analytical methods developed to measure reactive compounds [55] summarized the results. The following methods (only the ones relevant for the parameters in Table 4) were developed:

- Measurement of hydrogen sulphide using Optical Feedback Cavity Enhanced Absorption Spectroscopy (OFCEAS)
- Pre-concentration gas chromatography pulsed discharge helium ionization detector for hydrogen sulfide, methanethiol, carbonyl sulfide and carbon disulfide

In CEN/TC 234 (gas infrastructure), a new work item proposal “Quality of gas – Hydrogen used in converted/rededicated gas systems” [7] is currently discussed. The proposed parameters are verified by German project results (HyQual) which have been consulted in combination with end-users" specifications. In the project, different sources of hydrogen have been evaluated, such as pyrolysis, steam reforming, electrolysis (Chlor-Alkali process and water electrolysis) and biological hydrogen production process. Many parameters given (Table 5) in this NWIP are deduced from EN 16726 [38].

Table 5 – Proposed parameters in the NWIP "Quality of gas – Hydrogen used in converted/rededicated gas systems"

Content or characteristic	CEN TC 234 NWIP (HyQual)
Hydrogen fuel index (minimum mole fraction)	98 cmol/mol
Carbon monoxide	1000 µmol/mol
Total sulphur (including H_2S)	10 mg / m^3
Hydrocarbon dewpoint	-2 ºC (dew point)
Water	50 mg / m^3
Oxygen	10 µmol/mol
Ammonia	10 mg/m^3
Halogenated	< 0.05 µmol/mol
Other impurities	Technically free

BSI has developed a fast-track standard (PAS 4444 - Guide to hydrogen-fired gas appliances [12]) to help form the basis for wide-scale standardization of hydrogen-fuelled appliances. The fast-track standard helps manufacturers regarding the safety and functionality of hydrogen-fuelled appliances such as boilers, cookers and fires. The specifications are given in Table 6.

Table 6 - Specifications in BSI PASS4444 [12]

Content or characteristic	BSI PAS 4444 (Hy4Heat)
Hydrogen fuel index (minimum mole fraction)	98 cmol/mol
Carbon monoxide	20 µmol/mol (ppm)
Hydrogen sulphide	≤ 3.5 µmol/mol
Total sulphur (including H_2S)	≤ 35 µmol/mol
Oxygen content	≤ 0.2 cmol/mol (molar)
Methane	≤ 1 cmol/mol (molar)

Carbon dioxide	
Total hydrocarbons	
Hydrocarbon dewpoint	-2 °C (dew point)
Water	-10 °C (dew point)
Argon	≤ 2 cmol/mol (molar)
Nitrogen	
Helium	
Wobbe Number range	42 – 46 MJ m^{-3}
Calorific value	11.11 – 12.11 MJ m^{-3}
Other impurities	*

*Shall not contain solid, liquid or gaseous material that might interfere with the integrity or operation of pipes or any gas appliance, within the meaning of regulation 2(1) of the Gas Safety (Installation and Use) Regulations 1998, that a consumer could reasonably be expected to operate

GERG (European Gas Research Group) is currently running a project on pre-normative research requirements for the introduction of hydrogen into our gas networks [56] in close cooperation with the European Commission's Energy Directorate and CEN Technical Committee TC234 (Gas Infrastructure) where one of the eight priority areas is gas quality. The project will run until November 2021.

4 CARBON DIOXIDE

4.1 CARBON CAPTURE

CO_2 emissions from many industries can be used for CO_2 capture and storage: cement plants (from calcination of carbonated materials), iron and steel plants, high-purity industrial sources (such as natural gas processing, hydrogen production, coal/gas-to-liquids and ammonia production), pulp and paper industry and biofuels production (bio-chemical and thermochemical production) are some examples. As for all gases discussed in the present study, the composition of the gas will vary depending among others, on the method of production and the raw materials. Matteo *et al*. listed relevant streams for CO_2 capture together with some indications about the composition of the streams with regards to CO_2 (10 to 30%) and other component and impurities (oxygen; O_2, nitrogen; N_2, sulfur oxides; SOx, nitrogen oxides; NOx, hydrogen; H_2, carbon monoxide; CO, water; H_2O) (the focus was on cement plants, iron and steel plants and refineries) . More recently, CO_2 stream composition data was compiled from existing literature (review reports, results from pilot, demonstration or commercial projects) by the expert group appointed by ISO/TC265 from WG5 "Cross-cutting issues", some conclusions are presented in ISO/TR27921:2020 [3]. Besides the impurities already named, other impurities are mentioned depending again on the origin of the CO_2 stream (including the raw materials); benzene, methanol, methane, chlorine, H_2S, COS, naphthalene, ammonia, amines, aldehydes and metals (Hg, Pb, Se, As, Mn, Ni).

The document ISO/TR27291:2020 [3] also describes the effects of the impurities present in the CO_2 stream on the storage (classified as physical, chemical, microbiological and toxicological). For example, impurities of the CO_2 stream can affect both the thermodynamic and transport properties (operating pressure, temperature, fluid density, safety considerations, fracture control and cloud dispersion). A study conducted by IEAGHG showed that the storage capacity is depending on the composition of the CO_2 stream as impurities will impact on the density of the CO_2 stream. Therefore, it is important to monitor the composition of the CO_2 stream.

To set specifications, it is necessary to understand which part of the CCS chain will constrain the CO_2 stream composition (Annex A, A.6, ISO/TR27291:2020 [3]). The required purity of the CO_2 stream delivered from the capture plant will mostly depend on the impurity levels that can be accepted by the transport, injection and storage operators.

Another important information found in ISO/TR27291:2020 [3] is a compilation of four recent specifications for CO_2; for the DYNAMIS project, the National Energy Technology Laboratory (NETL) based on a review of 55 CO_2 specifications, the CarbonNet project and specifications presented by IPCC and Kinder Morgan (Table 7). However, ISO/TR 27291.2020 [3] concludes that even if identifying impurity concentrations and impacts is a cross-cutting issue for integrated CCS projects, it is difficult to set common threshold and threshold are case-specific for two main reasons:

1) Site-specific risk studies are usually carried out by operators for a particular project
2) Interactions between impurities and with the surroundings might result in impacts different from those of a single impurity

Table 7 – CO_2 specifications given in ISO/TR27291:2020 [3]

µmol/mol	DYNAMIS [57]	NETL [58]	Literature review [59]*	CarbonNet [60]
H_2O	500	730/500	20-650	100
H_2S	200	100	20-13000	100
CO	2000	35	10-5000	900
O_2	<40000	40000/10	100-40000	20000
NO_x	100		20-2500	250
SO_x	100		10-50000	200

*Another study from Hua and Neville [61]citing the same source reported even lower limits for H_2O (10 ppm) and for H_2S (10 ppm)

However, more detailed specifications (Table 8) have been given in the deliverable D4.9 of the CAESAR project (Carbon-free Electricity by SEWGS: Advanced materials, Reactor, and process design. The report presents a compilation of information from previous projects (including those from the European Benchmarking Task Force, EBTF) [16].

Table 8 – Limits in the CO2 stream found in the CAESAR project [16].

	EBTF	Aquifer	Enhanced oil recovery
CO_2	>90 vol-%	>90 vol-%	>90 vol-%
H_2O	<500 ppm-vol	<500 ppm	<50 ppm-vol
H_2S	<200 ppm-vol	<1.5 vol-%	<50 ppm-vol
NOx	<100 ppm-vol	-	-
SOx	<100 ppm-vol	-	<50 ppm-vol
HCN	<5 ppm-vol	-	-

COS	<50 ppm-vol	-	<50 ppm-vol
RSH	<50 ppm-vol	-	>90 vol-%
N_2	<4 vol-%	<4 vol-%	<4 vol-%
Ar	<4 vol-%	<4 vol-%	<4 vol-%
H_2	<4 vol-%	<4 vol-%	<4 vol-%
CH_4	<2 vol-%	<4 vol-%	<2 vol-%
CO	<0.2 vol-%	<4 vol-%	<4 vol-%
O_2	<100 ppm-vol	<4 vol-%	<100 ppm-vol

ISO/TR27915:2017 [5] presents a review of publicly available literature identifying materially relevant issues and options relating to "good practices" for quantifying and verifying greenhouse gas emissions and reductions at the project level. Its scope covers all components of the CCS chain including. capture, transport and storage.It also features a lifecycle assessment approach to estimating project level emissions and emission reductions from project assessment, construction and operations, through to completion and post-closure activities. This document also considers the composition of the CO_2 stream, including its purity, and requirements for measuring and verifying the physical and chemical state of the CO_2 stream in CCS projects. Claus 7.4.6 is dedicated to impurities in the CO_2 stream and recommends the measurement of the exact amount of CO_2 in the stream but also the content of impurities as they are likely to have physical or chemical effects in the behaviour of the CO_2 stream, on surface facilities or on the storage system. The impurities mentioned are N_2, O_2, H_2, Ar (main impurities), CH_4, CO, H_2O (in lesser quantities) and SO_2, NO_2, H_2S, Hg and other metals and trace organics such as benzene (very low concentration).

ISO27913:2016 [4] specifies additional requirements and recommendations not covered on existing pipeline standards for the transportation of CO_2 streams from the capture site to the storage facility where it is primarily stored in a geological formation or used for other purposes (e.g. EOR or CO_2 use). Impurities in the CO_2 stream can result in negative impacts on the pipeline integrity. Impurities have impacts on the thermodynamic properties and the viscosity of the CO_2 stream which cannot be predicted out of the properties of pure CO_2. Impurities can cause corrosion or generate chemical reactions. Annex A provides a list of impurities in the CO_2 stream O_2, H_2O, N_2, H_2, SOx, NOx, H_2S, HCN, COS, NH_3, amines, aldehydes, particulate matter). Indicative levels of CO_2 impurities with factors driving these levels are given in the standard (Table 9).

Table 9 – Indicative levels of CO_2 impurities and factors driving these levels, ISO27913:2016

Species	levels	Factors
CO_2	>95 vol-%	
H_2O	20 to 630 ppm <200 ppm	Corrosion, cross chemical reactions, hydrate formation
$H_2+N_2+Ar+CH_4+CO+O_2$	<4 vol-%	
H_2	<0.75 vol-%	Decompression behaviour of the CO_2 stream
N_2	<2 vol-%	Affects decompression behaviour of the CO_2 stream, and solubility of water in the CO_2 stream
Ar	-	Decompression behaviour of the CO_2 stream
CH_4	-	Affects decompression behaviour of the CO_2 stream, and

		solubility of water in the CO_2 stream
CO	<4 vol-%	Cracking, health and safety
O_2		Cross chemical reactions
H_2S	<200 ppm	Corrosion, cross chemical reactions, health and safety Affects solubility of water in the CO_2 stream
SO_2	<100 ppm-vol (health and safety) <50 ppm-vol (corrosion)	Corrosion, cross chemical reactions, health and safety
NO_2	<100 ppm-vol (health and safety) <50 ppm-vol (corrosion)	Corrosion, cross chemical reactions, health and safety
Amine		Cross chemical reactions
Methanol		Cross chemical reactions
Ethanol		Cross chemical reactions
Glycol		Cross chemical reactions
C2+	<2.5 vol-%	Condensation

A recent report [62] from the CCUS projects network (financed by the EC) has compiled carbon dioxide specifications for transport in different tables; including CO_2 quality recommendations for ship transport, Kinder-Morgan specification for supply to CO2-EOR, adapted DYNAMIS CO_2 quality recommendation and pipeline entry specifications for CO_2 (taken from Teesside and CarbonNet). The specifications given in this report are summarized in Table 10:

Table 10 – Different specifications summarized in [62]

Species	Ship transport (Aspelund 2010)	Kinder-Morgan	Adapted DYNAMIS	CarbonNet lower	Teesside
CO_2	>99.7 vol-%	>95 vol-%	>95.5 vol-%	>93.5 vol-%	>95 vol-%
H_2O	<50 ppm-vol	20 ppm-vol	<500 ppm-vol	<100 ppm-vol	<50 ppm-vol
H_2S	<200 ppm-vol	<0.9 vol-%	<200 ppm-vol	<100 ppm-vol	<200 ppm-vol
Total sulphur [S]	-	<35 ppm-vol	-	-	-
H_2	<0.3 vol-%*	-	<4 vol-%*	<2 vol-%*	<1 vol-%
N_2	<0.3 vol-%*	<4 vol-%	<4 vol-%*	<2 vol-%*	<1 vol-%
Ar	<0.3 vol-%*	-	<4 vol-%*	<2 vol-%*	<1 vol-%
CH_4	<0.3 vol-%*	<0.7 vol-%**	<2 vol-%	<2 vol-%*	<1 vol-%
CO	<2000 ppm-vol	<1000 ppm-vol	<2000 pmm-vol	<900 ppm-vol	<2000 ppm-vol
O_2	-	<50 ppm-vol	<100 ppm-vol	-	<10 ppm-vol
SOx	-	-	<100 ppm-vol	<200 ppm-vol	<100 ppm-vol
NOx	-	-	<100 ppm-vol	<250 ppm-vol	<100 ppm-vol
Glycol	-	<0.3 gal/MMcf	-	-	-
Ammonia					<50 ppm-vol
C2+	-	<2.3 vol-%	-	<0.5%***	<2 vol-%

*all non-condensable gases (include O_2, CH_4, N_2, Ar and H_2)
**included in hydrocarbons
*** other than CH_4

A project has specifically studied the post-capture CO_2 management options for the cement industry [63]. The authors concluded that CO_2 utilization should always be considered in combination with storage, for the cement industry, the fraction of CO_2 used in a full scale CCUS implementation is expected to be lower than 10%. Examples of utilization given in the report are production of ethanol, production of polyol. In the section below, we reviewed CO_2 utilization and related specifications when available.

4.2 CARBON UTILIZATION

CO_2 can also be physically and chemically employed in the various fields of chemical, biological, and food processes [64]. Zhang *et al.* [65] recently reviewed the carbon dioxide utilization technologies including mineralization, biological utilization, food and beverage, energy storage and chemical production. Those processes are at different stages of development and demonstration.

CO_2 can be used for the sustainable production of chemicals (urea, formic acid, methanol, cyclic carbonates, salicylic acid) or even fuels. On Figure 1 from [66], the different products from CO_2-based syntheses together with the degree of maturity of the technologies (commercial, demonstration of lab scale) and applications for the final product are presented.

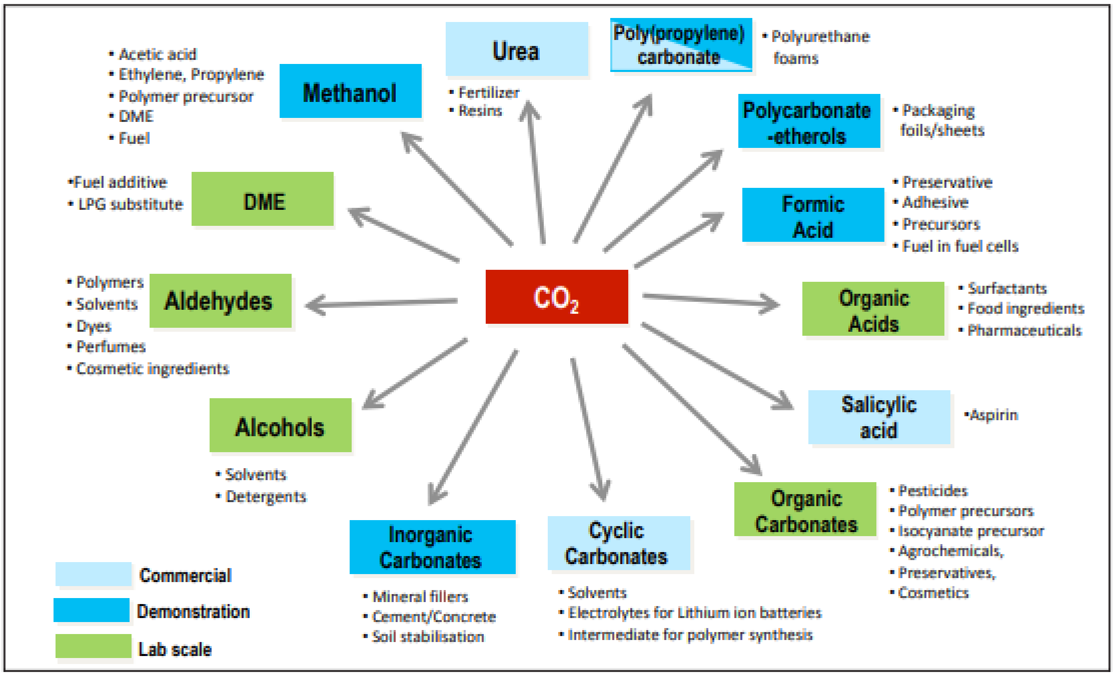

Figure 1 – Products from CO_2-based syntheses

In the urea synthesis reaction, CO_2 reacts with ammonia to form urea [66] according to the reaction:

$$CO_2 + 2\ NH_3 \rightarrow NH_2\text{-}CO\text{-}NH_2 + H_2O$$

Urea can be used as a nitrogen fertilizer or as a starting material in the chemical industry for the production of other chemical products, such as urea resins. Urea resins are useful as adhesives and for their impregnation and insulation properties.

The synthesis of salicyclic acid from phenol using CO_2 is called the Kolbe Schmitt reaction (or process)

The synthesis of cyclic carbonates is done by reacting epoxides with CO_2. Cyclic carbonates are used as solvents, electrolytes for lithium-ion batteries and as intermediates in a variety of polymer syntheses.

Methanol can be produced by catalytic hydrogenation of CO_2 according to the reaction:
$CO_2 + 3\ H_2 \rightarrow CH_2OH + H_2O$
The hydrogen is either produced through the electrolysis of water or utilization of by-product hydrogen. The CO_2 gas should contain a minimum of 99% CO_2 at the inlet to the reactor [67].

The hydrogenation of carbon dioxide leads initially to the formation of formic acid (HCOOH). Formic acid is an industrial chemical that is used for neutralizing alkaline reaction mixtures, as a preservative in the food industry, for tanning in the leather industry, and for bonding polyamide in the plastics industry. There is also the possibility of generating hydrogen from formic acid for use in fuel cells

Industrial CO_2 emissions can be used through mineralization processes to form various products. Mineralization processes typically require source materials such calcium, magnesium, or silicate-bearing rocks that can react with CO_2 to form useful minerals. These source materials can come from natural rocks or from industrial wastes such as mine tailings.
One example of mineralization is the reaction between silicates, mineral oxides and CO_2 to form minerals, such as carbonates, which can be used in various building material applications.
For example, through its reaction with silicates and mineral oxides, CO_2 can be incorporated in inorganic carbonates, which can be used, for example, in construction materials like cement, which is the binder used in concrete

CO_2 can be used as an acidifying agent in the beverage and food industry (production of carbonated drinks, de-oxygenated water, milk products, food preservation). But here the CO_2 purity is very important. Several standards and documents containing specifications for CO_2 for these applications have been produced.

EN936:2013 [11] prepared by the technical committee CEN/TC164 “water supply” is applicable to carbon dioxide used for treatment of water intended for human consumption. It describes the characteristics of carbon dioxide and specifies the requirements (Table 11) and corresponding analytical methods for carbon dioxide.

Table 11 – CO_2 specifications in EN936:2013 [11]

Compounds	Limits	Test methods
Carbon dioxide	>99.9 vol-%	Absorption in KOH GC (ISBT
Moisture	<50 ppm-vol	GC
Ammonia	<2.5 ppm-vol	GC
Oxygen	<30 ppm-vol	GC
NOx	<2.5 ppm-vol each	GC
Non-volatile residue (particulates)	<10 ppm-weight	GC
Non-volatile organic components (oil and fat)	<5 ppm-weight	GC

Total volatile hydrocarbons (calculated as methane)	< 50 ppm-vol, <20 ppm-vol non-methane	GC
Acetaldehyde	<0.2 ppm-vol	GC
Benzene	<0.02 ppm-vol	GC
Carbon monoxide	<10 ppm-vol	GC
Methanol	<10 ppm-vol	GC
Hydrogen cyanide	<0.5 ppm-vol	GC
Total sulfur (as S) H2S COS	<0.1 ppm-vol if over then <0.1 ppm-vol <0.1 ppm-vol	GC
Taste and odour in water	Acceptable to consumers and no abnormal change	

EN936:2013 refers to the recommendations from the document BVG-00001 [15] published by ISBT (International Society of Beverage Technologists) for the sampling and test methods for CO_2. The only method recommended for analyzing the impurities is gas chromatography (no detection method is specified).

Document 70-17 [13] from EIGA describes the specification requirements (Table 12) for liquid carbon dioxide in bulk production tanks or intermediate storage tanks at the gas supplier's depots for use in foods and beverages and is applicable to carbon dioxide used in beverage or in food when carbon dioxide is in direct contact with food or with beverage such as an ingredient or additive. The limits are quite similar to those in EN936:2013 [11] but more stringent for water and include phosphine (if CO_2 is produced from phosphate rock sources) and hydrogen cyanide (if CO_2 is produced from coal gasification sources). Table 12 also includes proposed analytical techniques for many of the parameters.

Table 12– EIGA limiting characteristics for CO_2 to be used in beverages for source specifications [13]

Compounds	Limits	Test methods
Carbon dioxide	>99.9 vol-%	Absorption in KOH GC (ISBT
Moisture	<20 ppm-vol	Hygrometry
Ammonia	<2.5 ppm-vol	
Oxygen	<30 ppm-vol	GC or dedicated analyser
NOx	<2.5 ppm-vol each	Chemiluminescence, colorimetric, colorimetric tube, MS, IR
Non-volatile residue (particulates)	<10 ppm-weight	Gravimetric
Non-volatile organic components (oil and grease)	<5 ppm-weight	Gravimetric, IR
Phosphine*	<0.3 ppm-vol	
Total volatile hydrocarbons (calculated as methane)	< 50 ppm-vol, <20 ppm-vol non-methane	GC or THC analyser
Acetaldehyde	<0.2 ppm-vol	GC, colorimetric tube, IR
Benzene	<0.02 ppm-vol	GC, MS, UV
Carbon monoxide	<10 ppm-vol	GC, colorimetric tube, IR
Methanol	<10 ppm-vol	GC, MS, colorimetric tube, UV, IR

Hydrogen cyanide**	<0.5 ppm-vol	Gas chromatography, mass spectrometry, calorimetric tube, infra-red spectroscopy
Total sulfur (as S) H_2S COS SO_2	<0.1 ppm-vol if over then <0.1 ppm-vol <0.1 ppm-vol <1 ppm-vol	UV fluorescence/ oxidiser, dedicated analysers, sulfur chemi-luminescence GC, UV fluorescence, colorimetric tube, MS, IR GC, MS, IR GC, colorimetric tube, MS, IR
Taste and odour in water	No foreign taste or odour	
Appearance in water	No colour or turbidity	
Odour and appearance of solid	No foreign odour or appearance	

In the EU legislation and JECFA [18], the current food additives CO_2 specifications are (E290) are given in Table 13:

Table 13 - Current food additives CO_2 specifications [18]

	Carbon dioxide, E290
Assay	>99 vol-%
Moisture	<52 ppm-vol (JECFA)
CO	<10 ppm-vol (< 10 µl/l, EC)
Total hydrocarbons	<50 ppm-vol (JECFA)
Oil	<5 mg/kg (EC) <10 ppm-vol (JECFA)
Acidity	15 ml of gas bubbled through 50 ml of freshly boiled water must not render the latter more acid to methylorange than is 50 ml freshly boiled water to which has been added 1 ml of hydrochloric acid (0,01 N) (EC)
Reducing substances, hydrogen phosphide and sulphide	915 ml of gas bubbled through 25 ml of ammoniacal silver nitrate reagent to which has been added 3 ml of ammonia must not cause clouding or blackening of this solution (EC)

JECFA – Joint FAO/WHO Expert Committee on Food Additives, (FAO - Food and Agricultural Organisation of the United Nations and WHO - World Health Organisation), www.fao.org

Other possible utilizations of CO_2 stream are related to the field of algae. Algae are famous for their relatively high growth rate and carbon capture ability. As other plants, algae capture the light energy to fuel the manufacture of sugars. Strategies to address concerns with CO_2 purity and flue gas contaminants can entail either working with algal strains that are able to handle high contaminant concentrations or improving flue gas treatment. Algae farmers could either select for or engineer algae species (extremophiles) that can tolerate a given flue gas composition or opt to adapt native strains growing naturally near the facility. Alternatively, algae farmers could also employ flue gas treatments, such as improved separations, desulfurization, pre-combustion nitrogen removal, and/or installation of heavy metal capture filtration or similar unit processes. Algae can be used to “clean up” CO_2 streams for example from biogas and biomethane facilities [64].

The Compressed Gas Association (CGA) has produced a document describing the specification requirements for gaseous, liquid and solid carbon dioxide [68]. The document gives limits (Table 14) for five different uses for carbon dioxide: medical/USP, general commercial uses (inerting, fumigation, propellant, food processing, beverages and dry ice – refrigeration) together with recommended analytical procedures. However, analytical procedures not listed in this specification are acceptable if agreed to by the supplier and the customer.

Table 14- GCA G-6.2 limits

	Medical/USP	General commercial uses	Food processing	Beverages	Dry ice, refrigeration
CO_2 identification	Pass		Pass		
CO_2 min vol-%	99	99	99.5	99.9	
Acetaldehyde ppm-vol		0.5	0.5		
Ammonia	25			2.5	
Acidity				To pass JEFCA test	
Benzene				0.02	
Carbon monoxide	10		10	10	
Carbonyl sulfide			0.5		
Hydrogen cyanide				None detected	
Methanol				10	
Nitric oxide	2.5		5 ($NO+NO_2$)	2.5	
Nitrogen dioxide	2.5		-		
Oxygen		50	50	30	
Phosphine				0.3	
Sulfur dioxide	5		5	1	
Total sulfur		0.5	0.5	0.1	
Total hydrocarbon content (as CH_4)		50	50	50 (incl 20 of NMHC)	
Hydrogen sulphide	1		0.5		
Color					White opaque

Non volatile residues (wt/wt)		10	10	10	500
Oil/grease (wt/wt)				5	
Odor/taste	Free of foreign odor or taste				
Water	200	32	20	20	
Dewpoint (ºC)	-36.1	-51.7	-55.6	-55.6	

Conclusion

For biomethane, hydrogen for heat and carbon dioxide for CCUS, method developments go hand in hand with the development of gas quality specifications. Quality specifications are usually designed to minimize risks associated with the utilization, storage and/or transport of the gas and include considerations regarding the possible effect of impurities on proper and safe functioning of appliances, on the integrity of the supply pipework (in particularly risk for corrosion and chemical reactions), on health and on the properties of the products (viscosity, thermodynamical properties etc.).

Specifications for biomethane have been produced in 2016 and 2017. The test methods proposed in these standards are mostly for offline methods developed for other matrices such as natural gas and air. These methods need to be validated properly for biomethane and possibly, new methods specifically for biomethane should be developed. This has been started in the project 16ENG05 Metrology for biomethane. There is also a need to develop and validate online methods specifically for ISO16723-1:2016. It is also possible that the specifications will evolve in a near future to include other parameters for example a limitation for terpenes.

For hydrogen for heat, the key existing documentary standard providing requirement for hydrogen quality is ISO14687:2019, however, a recent report [1] concludes that new hydrogen purity specifications for use in domestic and commercial heating applications are needed and a new work item proposal entitled Quality of gas – Hydrogen used in converted/rededicated gas systems is under development. Available analytical techniques suitable for measurement of impurities in hydrogen are listed in the standard ISO21087:2019 or in reviews [43] [54]. However, the lists are based on requirements for the grade D (PEM fuel cell road vehicle application) which has more stringent limits than for grades A or E. Once specifications are specifically set for hydrogen for heat applications, it will be necessary to review the analytical methods fit-for-purpose for the new requirements.

For carbon dioxide for CCS, currently, no universally agreed upon specification for CO_2 quality exists. ISO/TR 27291.2020 concludes that even if identifying impurity concentrations and impacts is a cross-cutting issue for integrated CCS projects, it is difficult to set common threshold. So far, impurities to quantify and associated threshold found in different documents (ISO27913, ISO/TR 27291.2020, EBTF…) vary from one document to the other. Therefore, there are currently no proposed test methods. Analytical methods need to be developed for the impurities most commonly mentioned and should preferably target the lowest threshold given in the documents mentioned in this study (Table 15).

Table 15 – Lowest thresholds for impurities for CCS

Compounds	Lowest threshold	References
H_2O	20 ppm-vol (10 ppm-vol)	[59] [4], ([61])
H_2S	20 ppm-vol (10 ppm-vol)	[59] ([61])
CO	10 ppm-vol	[59]
O_2	100 ppm-vol	[59] [18]
NOx	20 ppm-vol	[59]
SOx	10 ppm-vol	[59]
HCN	5 ppm-vol	[18]
COS	50 ppm-vol	[18]
N_2	0.3 vol-%*	[62]
Ar	0.3 vol-%*	[62]
H_2	0.3 vol-%*	[62]
CH_4	0.3 vol-%*	[62]
H_2+N_2+Ar+CH_4+O_2	0.3 vol-%	[62]
Amine	*	[4]
Methanol	*	[4]
Ethanol	*	[4]
Glycol	2.5 lb/MMcf (15 ppm-vol?)	[62]
C2+	0.5 vol-%	[62]
Ammonia	50 ppm-vol	[62]

**all non-condensable gases (include O_2, CH_4, N_2, Ar and H_2)
**No value

A number of specifications exist for different CO_2 utilizations. They are summarized in Table 16. In the second column, the most stringent limits for the different specifications are also reported. For most of the parameters, the most stringent limits are those from EN936 and EIGA70/17 (intended for human consumption).

Table 16 – Summary of the specifications for CO2 utilization

	Most stringent	EN936	EIGA 70/17	E290	GCA G-6.2				
		treatment of water intended for human consumption	Beverages	Food additives	Medical/USP	General commercial uses	Food processing	Beverages	Dry ice, refrigeration
CO_2 identification					Pass		Pass		
CO_2 min vol-%	99.9	99.9	99.9	99	99	99	99.5	99.9	
Acetaldehyde ppm-vol	0.2	0.2	0.2			0.5	0.5		

Ammonia	2.5	2.5	2.5		25			2.5	
Acidity			-	Test in boiled water				To pass JEFCA test	
Benzene	0.02	0.02	0.02					0.02	
Carbon monoxide	10	10	10	10	10		10	10	
Carbonyl sulfide	0.1	0.1	0.1				0.5		
Hydrogen cyanide	0.5	0.5	0.5					None detected	
Methanol	10	10	10					10	
Nitric oxide	2.5	2.5	2.5		2.5		5 (NO+NO$_2$)	2.5	
Nitrogen dioxide	2.5	2.5	2.5		2.5		-		
Oxygen	30	30	30			50	50	30	
Phosphine	0.3	-	0.3					0.3	
Sulfur dioxide	1	-	1		5		5	1	
Total sulfur	0.1	0.1	0.1			0.5	0.5	0.1	
Total hydrocarbon content (as CH$_4$)	50 (incl 20 of NMHC)	50 (incl 20 of NMHC)	50	50		50	50	50 (incl 20 of NMHC)	
Hydrogen sulphide	0.1	0.1	0.1		1		0.5		
Color		-							White opaque
Non volatile residues (wt/wt)	10	10	10			10	10	10	500
Oil/grease (wt/wt)	5	5	5 ppm	5 mg/kg (EC) 10 ppm (JECFA)				5	
Odor/taste		Acceptable to consumers and no abnormal change	No foreign taste or odor						Free of foreign odor or taste
Apperance in water			No clour or						

			turbidity						
Odour and appearance of solid			No foreign odour or appearance						
Water	20	50	20	52	200	32	20	20	
Dewpoint (ºC)	-55.6				-36.1	-51.7	-55.6	-55.6	

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Bulk Carbon Dioxide: Quality & Food Safety Guidelines and Analytical Methods and Techniques Reference
Last Updated: November 2019
BVG-00001

This publication establishes production and feed gas considerations, finished product impurity levels, and analytical method recommendations for Beverage Grade Bulk Carbon Dioxide. The analytical methods addendum to this guideline outlines analytical methods and considerations for finished product and impurities. The scope of this document covers various feed gas sources, production technologies and considerations, and finished bulk product testing and analysis.

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