



CARBON DIOXIDE SOURCE QUALIFICATION QUALITY STANDARDS AND VERIFICATION

IGC Doc 70/08/E

Revision of IGC Doc 70/99/E

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1 Introduction

This document has been prepared by an ad hoc working group of the European Industrial Gases Association (EIGA) working in conjunction with the Compressed Gases Association of America (CGA) and the International Society of Beverage Technologists (ISBT). The document has been prepared to provide guidance on standards for source qualification and specification of bulk carbon dioxide for use in foods and beverages.

2 Scope

This document describes the specification requirements for liquid carbon dioxide in bulk production tanks or intermediate storage tanks at the gas suppliers depots for use in foods and beverages. These specifications do not apply to CO₂ used as processing aid, e.g. food freezing, for cooling such as dry ice.

The document provides recommendations for good practice in order to provide guidance on the key characteristics for the quality and purity of carbon dioxide for use in foods and beverages and the quality assurance and quality control procedures necessary to ensure compliance. Individual needs however, may dictate the application of additional requirements negotiated between carbon dioxide suppliers and carbon dioxide users.

The document also provides recommendations for the qualification of plants used to produce carbon dioxide for use in foods and beverages. These recommendations are also intended to assist carbon dioxide suppliers to achieve compliance with applicable regulatory standards such as EC Directive 96/77/EC, 98/83/EC, INS No. 290, US Good Manufacturing Practice (21CFR10) and local governmental requirements, JECFA – Joint FAO/WHO Expert Committee on Food Additives.

3 Classification and Definition

Carbon dioxide (CO₂) is a colourless, odourless, non-combustible gas. Carbon dioxide above the triple point temperature of -56.6°C and below the critical point temperature of 31.1°C can exist in both a gaseous and a liquid state.

Raw Gas means the CO₂ feed gas before the CO₂ purification system.

Unprocessed (other than compression and or cooling) gas that flows from a source to the plant.

Source plant is any plant with one or more processes generating gaseous CO₂ usually as a by product or of natural sources.

CO₂ plant is any installed facility that is capable of producing liquid CO₂ meeting industry product specifications.

Bulk liquid carbon dioxide is commonly maintained as a refrigerated liquid and vapour at pressures between 1230 kPa (approx. 12 bar) and 2557 kPa. (Approx. 25 bar). Carbon dioxide may also exist as a white opaque solid with a temperature of -78.5°C at atmospheric pressure.

Warning: High concentrations of carbon dioxide (10 % or more) can asphyxiate quickly without warning with no possibility of self – rescue regardless of the oxygen concentration.

4 Limiting Characteristics

Table 1 (see Appendix A) is the maximum concentration of the listed components in ppm v/v (unless otherwise specified) for liquid carbon dioxide to be suitable for use in foods and beverages. In this document ideal gas behaviour is assumed when expressing composition in terms of ppm by volume.

Carbon dioxide is a by-product of many different natural and chemical processing mechanisms. This capability of multiple source types makes it unique in the industrial gas market. The variation of sources results in a variety of specific impurities that may be anticipated to be present in carbon dioxide. Typical sources and their respective anticipated components are listed in table 2 (see Appendix B). The levels of these trace impurities in addition to the limiting characteristics given in table 1 (see Appendix A) shall be assessed.

4.1 Levels of the Components

Table 1 gives maximum/ minimum concentrations for the key characteristics required to ensure that a finished beverage/ foodstuff is in compliance with applicable regulatory requirements and that the sensory characteristics of the product are maintained and not compromised.

4.1.1 Levels of the unlisted components

There may be other compounds as yet unknown or undetected in some carbon dioxide sources. The supplier and customer may assign acceptable levels for these potential compounds. Additionally established and published regulations may be used to define reasonable and prudent levels e. g. National Primary and Secondary Drinking Water Regulations (NPSDWR), &EEC315/93 + EC Directive 98/83/EC.

4.1.2 Method of calculating the level of a component in carbon dioxide for beverage applications

This publication provides a method for calculating a component's level of contribution to the beverage product from its concentration level in the carbon dioxide.

- a) It is recognised that trace impurities are present in the carbon dioxide and are assumed, for the purposes of this calculation, that they are consumed with the beverage product. The following points expand further:
- All of the components in the liquid carbon dioxide are assumed to be present in the gaseous carbon dioxide.
 - When carbon dioxide is put into a liquid, all of the impurities are assumed to remain solution and are consumed.
- b) To determine the contribution of a component in carbon dioxide used for these applications, the following assumptions are made:
- For beverages, the carbon dioxide concentration absorbed in the beverage is based on the known volumes bubbled through the liquid.

4.1.3 General formula

- a) y volume of carbon dioxide is used to carbonate one volume of liquid.
Full carbonation of water needs 8 g/l carbon dioxide and this concentration is used to determine the worst case scenario.
- b) The volume occupied by one mole of any substance in vapour-form or gas (reduced to 0°C and 1 atmosphere/760 torr or 1013 mbar) is equal to 22.414 litres assuming ideal gas behaviour.
- c) Mole is the molecular weight of a substance expressed in grams; for example, a mole of carbon dioxide weighs 44.01 grams, a mole of toluene weighs 92.14 grams, etc.
- d) Using C as the concentration of a component (ppm v/v or µl/l) in carbon dioxide and M as the molecular weight of that component, the concentration of that component (X mg/l) in the beverage is calculated by the following formula:

$C \mu\text{l/l} \times (M \text{ g} / 22.414 \text{ l}) \times V \times 10^{-3} = X \text{ mg/l}$ impurity in the carbon dioxide-
8 g CO₂ / l beverage are (22,414 l x 8 g / 44,01 g) CO₂ / l bev. = 4,07 l CO₂ / l beverage.
-> Impurity in beverage is X mg/l x 4,07 l.

5 Plant and Process Qualification

It is the responsibility of the company selling liquid carbon dioxide to the food and beverage industry, to ensure that qualified sources of carbon dioxide are used.

To be qualified for supply of liquid carbon dioxide to the food and beverage segment, the source operator shall fulfil all legal requirements as described in the current European and national food and beverage legislation (ref. EIGA doc 125/xx).

In addition, the liquid carbon dioxide produced by the source operator shall consistently meet the purity criteria listed in table 1

In accordance with legal requirements each supplier should implement a HACCP – system according to article 5 of Regulation (EC) 852/2004 including the following steps.

5.1 Source Evaluation

The supplier should perform an analysis of the source raw gas stream before design of the purification plant. During design the process controls required to ensure that carbon dioxide is produced according to the specification must be determined. The initial assessment of the raw gas source will give an indication of the normal variations in the composition of the raw gas. This may be used to select the components to be analysed and the frequency of regular analysis. Such an assessment should include a broad screening by chemical analysis, of components that could possibly be present as impurities for the type of source or introduced as contaminants in the process. The specific impurities listed in Table 2 (see Appendix B) for the generic sources must be assessed on a periodic basis or in case of process change to ensure that the impurity concentrations in the raw gas are as per the plant design assumptions. The detection level should be the same as that used for analysis of the final product.

5.1.1 Chemical Process plants as CO₂ Sources

The CO₂ raw gas is taken from different sources, as per table 2

In selection of a source as a possible raw gas stream for a CO₂ plant, it is necessary to assess the raw gas production process and the process feed stock.

The results of the raw gas analyses should be discussed with the process plant /source operator, to check if the raw gas composition could change under normal operation. The process operator should also inform the CO₂ plant, if there are changes in the process or its feed stock, which could affect the CO₂ quality.

5.1.2 Natural wells / Geothermal sources

The CO₂ raw gas of natural wells needs to be assessed in detail. The geological source and possible changes of components which may be found in the raw gas, particularly in case of variation of extraction, needs to be taken into consideration.

5.1.3 Fermentation sources

CO₂ raw gas from fermentation needs a detailed assessment to account for potentially larger variability than process sources.

The composition of the raw gas can vary due to apparently minor changes in the feedstock caused by geographical variations or growing conditions.

5.2 Production Qualification Tests and Design Validation

All carbon dioxide production facilities supplying carbon dioxide to food and beverage customers must be proven by analysis of all the key characteristics in Table 1 (Appendix A), plus appropriate components identified from Table 2 (Appendix B), to be capable of meeting the specification. This analysis may be a single analysis of a new facility or a series of analyses at a frequency determined by the supplier or by agreement with the customer.

A risk assessment (Refer to EIGA doc 125) should be used to identify key process controls required to ensure compliance with the specification. This assessment may be conducted by various methods¹. The effectiveness of these process controls may be assessed directly by chemical analysis, by the use of process tracers or by the use of process control instrumentation e.g. flow switches to verify operation of water scrubbers, temperature controls on catalytic oxidation systems, pressure and flow controls on stripping columns. The operation of the plant should be reviewed on a regular basis and be subject to periodic maintenance to ensure that the plant is in good condition.

5.3 Quality Control/ Quality Assurance

Each facility producing carbon dioxide for the food and beverage industry should have a documented system for quality management following the model in the ISO 9000 series of standards. In addition ISO 22000 is recommended for a food safety management system. Whilst preferable, it is not essential for this to be accredited by a third party.

The quality control and quality assurance procedures described by this document only apply to the carbon dioxide production sources. The EIGA documents listed in references below should be consulted.

The supplier should assure that carbon dioxide supplied to the food and beverage industry meets the specification given in Table 1 (Appendix A) plus appropriate components identified from Table 2 (Appendix B). The frequency of analysis required to prove compliance shall be determined by the supplier although table 3 may be used as a guide.

6 Quality control in CO₂ production

The CO₂ raw gas composition will determine the design of the plant, especially the purification steps and procedures and also the analytical controls during the process.

The purification process will need analytical controls for the process, if no other relevant parameters can be used, to assure that the purification step is working as intended.

Analytical controls during the process may be continuous using on-line instruments or based on spot checks. This choice and the selection of the frequency for checks will depend on:

- a) the component to be measured
- b) the likely concentration of the component
- c) the importance of the component to the perceived quality of the CO₂
- d) the ease of measurement
- e) risk assessment of the purification process designed to remove the component to acceptable levels.
- f) regulatory mandates and/or individual guide.

The frequency of checks will vary depending on consideration of these factors and may typically be from one per hour to two per year for components not analysed by continuous monitoring instruments.

7 Finished product analysis and release

7.1 CO₂ storage tank at the plant

The CO₂ is liquefied and pumped (flow) into one or more storage tanks. At some CO₂ plants it is possible to use each tank (or a cluster of tanks) as a batch (ref EIGA doc 125). This gives the possibility to release product based on analysis of the storage before the storage is used for filling of the tankers. The analysis of a batch should normally refer to the compounds found relevant from the raw gas assessment, and user requirements. The batch analysis can reduce the online-analysis in the plant to a minimum.

¹Acceptable methods could include Failure Mode Effect Analysis FMEA or Hazard Analysis by Critical Control Points (HACCP)

However, many plant storage tanks are operated in a continuous manner and batch analysis is not practical. Conformity of the storage is assured by analysis of the incoming product to the tank and/or regular analysis of the stored CO₂. Release of product may in this case be based on process control data showing consistent compliance, together with daily checks of key parameters

Suggested frequency of sampling and analysis against EIGA guideline specification is given in table 3.

In case of non-conformity, appropriate quality assurance routines have to be implemented in order to stop tanker filling and delivery and to take corrective and preventive actions.

7.2 CO₂ intermediate storage tanks (depots)

The conformity of the storage is assured by importing into the tank only product which complies to this specification. Compliance check and release of product according to this specification may be accomplished by total control of the release quality of incoming product, but also by performing analysis directly on product at intermediate storage, and release the product based on these tests.

8 Third party laboratory checks

Where possible it should be sampled and analysed by a test-laboratory independent from the production plant. This gives the possibility to cross-check the results of the production plant.

9 Frequencies

Table 3 is a guide to the analytical frequencies but individual application is dependant on the risk assessment.

10 Analytical Methods

The analytical methods used to prove compliance with the specification are attached as Appendix C.

Alternative methods may be used if these are validated as being at least equivalent to those in Appendix C.

The sample shall be taken from the liquid phase of the bulk storage tank or from the liquid carbon dioxide product stream from the production plant. Where the sample is taken in a cylinder then the cylinder shall be at room temperature prior to analysis and the phase of the sample cylinder to be analysed for various components is given in Appendix C.

APPENDIX A: Table 1

EIGA LIMITING CHARACTERISTICS

FOR CARBON DIOXIDE FOR FOODS AND BEVERAGES.

<u>Component</u>	<u>Concentration</u>
Assay	99.9% v/v min.
Moisture	50 ppm v/v max. (20 ppm w/w max.)
Ammonia	2.5 ppm v/v max.
Oxygen	30 ppm v/v max.
Oxides of Nitrogen (NO/NO ₂)	2.5 ppm v/v max. each
Non-volatile residue(particulates)	10 ppm w/w max.
Non-volatile organic residue (oil and grease)	5 ppm w/w max.
Phosphine ***	0.3 ppm v/v max
Total volatile hydrocarbons (calculated as methane)	50 ppm v/v max. of which 20 ppm v/v max non-methane hydrocarbons.
Acetaldehyde	0.2 ppm v/v max.
Benzene	0.02 ppm v/v max.
Carbon Monoxide	10 ppm v/v max.
Methanol	10 ppm v/v max.
Hydrogen Cyanide*	0.5 ppm v/v max
Total Sulphur (as S) **	0.1 ppm v/v max.
Taste and Odour in Water	No foreign taste or odour

* Analysis necessary only for carbon dioxide from coal gasification sources

** If the total sulphur content exceeds 0.1 ppm v/v as sulphur then the species must be determined separately and the following limits apply:

Carbonyl Sulphide	0.1 ppm v/v max.
Hydrogen Sulphide	0.1 ppm v/v max.
Sulphur Dioxide	1.0 ppm v/v max.

*** Analysis necessary only for carbon dioxide from phosphate rock sources

Where carbon dioxide complies with the specification then by definition the requirements for acidity and reducing substances as required by European Law are met.

APPENDIX B: Table 2

Possible Trace Impurities by Source Type (Excluding Air Gases and Water)

Note The source types are generic sources and there are variations in individual processes. Therefore, the supplier should assess whether or not all of the components listed are applicable to the actual plant.

Component	Combustion	Wells/ Geothermal	Fermentation	Hydrogen Ammonia or	Phosphate Rock	Coal Gasification	Ethylene Oxide	Acid Neutralisation
Aldehydes	√	√	√	√		√	√	
Amines	√			√				
Benzene	√	√	√	√		√	√	√
Carbon Monoxide	√	√	√	√	√	√	√	√
Carbonyl Sulphide	√	√	√	√	√	√		√
Cyclic Aliphatic Hydrocarbons	√	√		√		√	√	
Dimethyl Sulphide		√	√		√	√		√
Ethanol	√	√	√	√		√	√	
Ethers		√	√	√		√	√	
Ethyl Acetate		√	√			√	√	
Ethyl Benzene		√		√		√	√	
Ethylene Oxide						√	√	
Halocarbons	√					√	√	
Hydrogen Cyanide	√					√		
Hydrogen Sulphide	√	√	√	√	√	√	√	√
Ketones	√	√	√	√		√	√	
Mercaptans	√	√	√	√	√	√	√	
Mercury	√	√				√		
Methanol	√	√	√	√		√	√	
Nitrogen Oxides	√		√	√		√	√	√
Phosphine					√			
Radon		√			√			√
Sulphur Dioxide	√	√	√	√	√	√		√
Toluene		√	√	√		√	√	
Vinyl Chloride	√					√	√	
Volatile Hydrocarbons	√	√	√	√		√	√	
Xylene		√	√	√		√	√	

APPENDIX C: Table 3

Control Frequencies

Frequencies Components	Online or Daily or Batchwise	Yearly **	When changes at the source	Notes
Raw gas Source			1	
Purity	1	1		
Dew point (moisture)	1	1		
Ammonia	2	1		
Oxygen	2	1		Daily if at critical level
Oxides of Nitrogen	2	1		
Non volatile residue (particulates)	2	1		
Non volatile organic residue	2	1		
Phosphine	2	1		Only if raw gas is from phosphate rock
Total volatile hydrocarbon	1	1		
Acetaldehyde	2	1		
Benzene	2	1		
Carbon Monoxide	2	1		
Methanol	2	1		Daily if at critical level
Hydrogen Cyanide	2	1		Only if raw gas is from coal gasification sources
Total Sulphur	2	1		
Taste and odour in water	1	1		
Others*	2	1		

1 Recommended minimum frequency

2 Analysis is not required at this frequency if a formal risk assessment has been undertaken which has concluded that the specified maximum level for each component in the CO₂ product cannot be exceeded in normal operation or in a failure mode.

* See table 2

** The yearly control is done as a general check by a test-laboratory, independent from the production plant.

APPENDIX D: Table 4

Analysis methods

Component	Phase *	Method
Assay	Liquid	Absorption in KOH : e.g. Ors/ Zahm Nagel, IR spectroscopy
Moisture	Liquid	Hygrometry – capacitance, electrolytic, piezo-electric ,cooled mirror,IR spectroscopy,colorimetric tube, quartz crystal
Oxygen	Vapour	Gas chromatography or dedicated analyser
Oxides of Nitrogen	Liquid	Chemiluminescence, colorimetric, colorimetric tube, mass spectrometry, infra red spectroscopy
Non Volatile Residue	Liquid	Gravimetric
NVOR	Liquid	Gravimetric, infra-red spectroscopy
Acetaldehyde	Liquid	Gas chromatography,infra red spectroscopy,colorimetric tube, infra red spectroscopy
Benzene	Liquid	Gas chromatography, mass spectrometry, UV spectroscopy,
Carbon Monoxide	Vapour	Gas chromatography, colorimetric tube, infra red
Methanol	Liquid	Gas chromatography, mass spectrometry, colorimetric tube,UV spectroscopy, infra red spectroscopy
Ethanol	Liquid	Gas chromatography, mass spectrometry, colorimetric tube, infrav red spectroscopy
Ketones	Liquid	Gas chromatography,mass spectrometry, infra red spectroscopy
Toluene	Liquid	Gas chromatography, mass spectrometry, infra red spectroscopy, UV spectroscopy
Xylene	Liquid	Gas chromatography, mass spectrometry, infra red spectroscopy, UV spectroscopy
Hydrogen Cyanide	Vapour	Gas chromatography, mass spectrometry, calorimetric tube, infra red spectroscopy
Ethylene Oxide	Vapour	Gas chromatography, mass spectrometry,colorimetric tube, infra red spectroscopy
Total Sulphur	Liquid	UV fluorescence/ oxidiser, dedicated analysers,sulphur chemi-luminescence
Carbonyl Sulphide	Liquid	Gas chromatography, mass spectrometry,infra red spectroscopy
Sulphur Dioxide	Liquid	Gas chromatography , colorimetric tube, mass spectrometry,infra red spectroscopy
Hydrogen Sulphide	Liquid	Gas chromatography, UV fluorescence, colorimetric tube, mass spectrometry,infra red spectroscopy
Heavy Metals	Liquid	Atomic absorption or inductively coupled plasma,colorimetric tube(for some metals)
Amines	Liquid	Gas chromatography,colorimetric tubes , infra red spectroscopy
Radon	Liquid	Mass spectrometry
Total Hydrocarbons	Vapour	Gas chromatography or THC analyser

* when analysed in a sample cylinder

APPENDIX E: References

EIGA document "Prevention of CO₂ Backfeed Contamination" (Doc 68/08/E) is to be referred to for guidance on ensuring the integrity of the distribution chain.

EIGA document "CO₂ Tanker Driver Manual" (Doc 56/08/E) gives guidance on the operation of CO₂ tankers.

EIGA document "Guide to the Supply of Gases for use in Foods" (Doc 125/06/E) is intended to establish an awareness of the particular legislative requirements as they apply to food gases and to offer advice as to how these requirements can be met.