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Standard Guide for
Purity of Carbon Dioxide Used in Supercritical Fluid Applications[1]

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INTRODUCTION

The rapid commercial development of carbon dioxide for use in supercritical fluid extraction (SFE) and supercritical fluid chromatography (SFC) has hastened the need to establish common purity standards to be specified by specialty gas suppliers. As a consequence of its isolation from petrochemical side-streams or as a by-product of fermentation or ammonia synthesis, carbon dioxide contains a wide range of impurities that can interfere with analytical quantification or instrument operation. This guide is intended to serve as a guide to specialty gas suppliers for testing the suitability of carbon dioxide for use in SFC and SFE applications.

1. Scope

1.1 This guide defines purity standards for carbon dioxide to ensure the suitability of liquefied carbon dioxide gas for use in SFE and SFC applications (see Guide E1449 for definitions of terms). This guide defines quantitation, labeling, and statistical standards for impurities in carbon dioxide that are necessary for successful SFE or SFC laboratory work, and it suggests methods of analysis for quantifying these impurities.

1.2 This guide is provided for use by specialty gas suppliers who manufacture carbon dioxide specifically for SFE or SFC applications. SFE or SFC carbon dioxide (CO_2) products offered with a claim of adherence to this guide will meet certain absolute purity and contaminant detectability requirements matched to the needs of current SFE or SFC techniques. The use of this guide allows different SFE or SFC CO_2 product offerings to be compared on an equal purity basis.

1.3 This guide considers contaminants to be those components that either cause detector signals that interfere with those of the target analytes or physically impede the SFE or SFC experiment.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D2504 Test Method for Noncondensable Gases in C_2 and Lighter Hydrocarbon Products by Gas Chromatography
D2820 Test Method for C Through C Hydrocarbons in the Atmosphere by Gas Chromatography (Withdrawn 1993)[3]
D3670 Guide for Determination of Precision and Bias of Methods of Committee D22
D3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)
D3687 Test Method for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method
D4178 Practice for Calibrating Moisture Analyzers
D4532 Test Method for Respirable Dust in Workplace Atmospheres Using Cyclone Samplers

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[1] This guide is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and Separation Science and is the direct responsibility of Subcommittee E13.19 on Separation Science.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

E260 Practice for Packed Column Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

E697 Practice for Use of Electron-Capture Detectors in Gas Chromatography

E1449 Guide for Supercritical Fluid Chromatography Terms and Relationships

E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

2.2 *CGA Publications:*[4]

CGA G-5.4 Standard for Hydrogen Piping Systems at User Locations

CGA P-1 Safe Handling of Compressed Gases in Containers

CGA P-9 The Inert Gases: Argon, Nitrogen and Helium

CGA P-12 Safe Handling of Cryogenic Liquids

CGA V-7 Standard Method of Determining Cylinder Valve Outlets Connections for Industrial Gas Mixtures

G-6 Carbon Dioxide

HB-3 Handbook of Compressed Gases

3. Classification

3.1 This guide covers the following four different classes of compounds:

3.1.1 *Liquid-Phase Contaminants*—These are materials dissolved in the CO_2 liquid phase that can be volatilized below 300 °C and resolved chromatographically using a gas chromatography (CG) column; and detected by either a flame ionization (FI) or electron capture (EC) detector (D). Species representative of this class include moderate (100 to 600) molecular weight hydrocarbons and halocarbons (oils and lubricants).

NOTE 1—Liquid-phase contaminant levels are defined in terms of the lowest limit of detector response (LLDR)[5] for FIDs or ECDs only, because they are the primary detectors used with SFE or SFC techniques. However, the purification procedures used by the gas supplier to remove FID- and ECD-responsive contaminants are assumed to be effective for contaminants responsive to other (for example, NPD, MS, IR, UV, etc.) detectors.

Because a wide variety of contaminants are found in liquid-phase CO_2 as a consequence of its source, full speculation of every impurity by the gas supplier is impractical. All liquid-phase contaminants are therefore quantified relative to two representative internal primary reference standards: hexadecane (HD or $C_{16}H_{34}$) for the FID and hexachlorobenzene (HCB or C_6Cl_6) for the ECD. Contaminant limits are defined on a mass basis for single peaks and for the sum of all detector responses.

3.1.2 *Moisture*—Although water is sparingly (<0.1 % weight) soluble in liquid-phase CO_2, more than 10 ppm of moisture may result in physical interference resulting from ice formation during SFC or SFE applications. A maximum limit of 1 ppm of water in the carbon dioxide will be considered acceptable.

3.1.3 *Gas-Phase Contaminants*—Gaseous, noncondensible molecules released upon vaporization of liquid CO_2 may act as interferences during SFC applications; this is less of a problem in SFE applications. Species representative of this class include oxygen and light hydrocarbons, such as methane, ethane, and propane. A combined maximum concentration in the gas phase of 10 ppm will be considered acceptable.

3.1.4 *Nonvolatile*—Materials that leave a nonvolatile (boiling point >250 °C) residue following the vaporization of liquid CO_2, such as small particles and high-boiling solutes, are detrimental to both SFE and SFC applications. Species representative of this class include nonchromatographicable hydrocarbons or halocarbon oils, greases, and inorganic particles (for example, silica). A maximum concentration of 1 ppm will be considered acceptable.

4. Purity Specifications for SFE or SFC Grade CO_2

4.1 This guide proposes the following minimum purity specifications for CO_2 for each of the classes of contaminants, based on the demands of currently practiced SFE or SFC techniques.

4.1.1 *Liquid-Phase Contaminants Specification:*

4.1.1.1 SFE grade carbon dioxide is intended to be used as an extraction solvent from which a significant concentration of self-contained contaminates is possible because relatively large (>50 g) amounts of carbon dioxide may be used. Because each impurity cannot be identified, a known amount of internal reference compounds (for example, HD and HCB) will be used during the analysis to quantify contaminants on a relative weight basis. Total contaminant levels will be expressed in ng of contaminant per g of CO_2 and defined as that amount of impurity that will produce a detector signal at the "typical" detection limits for an FID or ECD found in 1.0 g of CO_2. The 1 g amount of carbon dioxide was selected as a convenient mass from which the chemist could relate carbon dioxide contamination levels with the amount of carbon dioxide required for his/her analysis by a simple ratio.

4.1.1.2 SFC grade carbon dioxide is intended to be used as a mobile phase material transferred directly from a chromatographic column to a detector (FID or ECD) without preconcentration (see Practice E355). Accepted internal reference compounds (for example, HD and HCB) will be used as surrogate contaminants. Contaminant levels will be expressed in ng of contaminant per g of CO_2 and will be defined as that amount which will produce a detector signal 20 times greater than the "typical" detection limit for FID and 25 times greater than an ECD at the lowest detectable limit for a single peak. A total of 200 times the lowest detectable limit will be set for all contaminants for a specific detector.

4.1.1.3 When specifying a FID response for SFE, the maximum amount of any one contaminant (that is, one peak in the chromatogram) will be 1 ng/g of liquid-phase CO_2. This is equivalent to 1 ppb on a mass basis, or 1 ppb w/w. The maximum amount of all FID-responsive contaminants (that is, the sum of all peaks in the chromatogram) will be 10 ng/g of liquid-phase CO_2 or 10 ppb w/w. Contaminant concentrations are expressed in terms of the equivalent response for hexadecane, the internal standard, regardless of the actual identity of the contaminant.

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[4] Available from Compressed Gas Association (CGA), 4221 Walney Rd., 5th Floor, Chantilly, VA 20151-2923, http://www.cganet.com.

[5] Poole, C. F., and Poole, S. K., *Chromatography Today*, Elsevier, 1991, p. 86.

4.1.1.4 When specifying an FID response for SFC, the generally accepted LLDR for a FID is 0.25 ng ± 0.1 ng for a single component with a signal-to-noise ratio of 3:1. Therefore, "20" × 0.25 ng = 5 ng to the detector (one peak), and "200" × 0.25 ng = 50 ng total detector response. If all 5 ng of the contaminant comes from 1 g of liquid-phase carbon dioxide, the single component impurity level would be 50 ppb. This assumes that 1 g of carbon dioxide arrives at the detector at one time, and the density of the CO_2 is 1 g/mL. Under typical SFC conditions of ∼400 atm and 75 °C, less than 0.1 g of CO_2 actually reaches the FID when using a 0.25 mm inside diameter column with a 15 s wide peak. Therefore, the contamination level acceptable for SFC applications would be less than 16 ppb on an absolute basis for a single peak (see Practice E594).

4.1.1.5 *ECD Detector*—For SFE, the maximum amount of any one contaminant (that is, one peak in the chromatogram) will be 0.2 ng/g of liquid-phase CO_2. This is equivalent to 0.2 ppb w/w, or 200 ppt w/w, on a mass basis. The maximum amount of all ECD-responsive contaminants (that is, the sum of all peaks in the chromatogram) will be 2 ng/g of liquid-phase CO_2 or 2 ppb w/w. Contaminant concentrations are expressed in terms of the equivalent response for hexachlorobenzene, the internal standard, regardless of the actual identity of the contaminant (see Practice E697).

4.1.1.6 For SFC applications, the ECD is >5 times more sensitive than the FID, assuming two halogen atoms per molecule. Therefore, the total concentration of a single ECD impurity is proposed to be 1 ng/g of CO_2 or 1 ppb. The total amount of ECD impurities considered acceptable is 10 ng/g of CO_2 or 10 ppb.

4.1.2 *Higher-Purity Materials*—The specifications and methodology proposed in this guide can be used to certify CO_2 materials with higher-purity specifications. To certify such materials, gas suppliers must vary (increase) the quantity of CO_2 collected and adjust the quantity of internal standard used for calibration. Contaminant concentrations are expressed in terms of the equivalent responses for the internal standards recommended above and reported on a mass basis relative to the mass of CO_2 collected. The applicable detector must be specified.

4.1.2.1 Minimum-purity CO_2 contains a total of 10 ng of FID-responsive contaminants per g of CO_2 (10 ppb w/w), with no single FID-responsive contaminant greater than 1 ng/g (1 ppb w/w). Higher-specification CO_2, for example, may contain a total of 1 ppb w/w of FID-responsive contaminants, with no single contaminant greater than 0.1 ppb w/w.

4.1.2.2 Gas suppliers are free to manufacture materials with purity specifications as stringent as they choose. SFC and SFE practitioners may use the purity reporting standards defined here as a basis for needs assessment and product comparison. No "grading" nomenclature is recommended in this guide.

4.1.3 *Moisture Specification*—The maximum amount of moisture acceptable in the carbon dioxide is 1 ppm (mole or volume basis).

4.1.4 *Gas-Phase Contaminants Specification:*

4.1.4.1 Gas-phase contaminants generally do not impede SFE or SFC experiments. However, to reduce the risk of inadvertent contamination, certain gas-phase contaminants should be specified and controlled.

4.1.4.2 *Oxygen (or Oxygen/Argon) Specification*—The maximum amount of oxygen (or unresolved oxygen/argon) acceptable is 5 ppm (mole or volume basis).

4.1.4.3 *Total Gas-Phase Hydrocarbons Specification*—The maximum amount of total gas-phase hydrocarbons (THCs) acceptable is 5 ppm (mole or volume basis), expressed as methane.

4.1.5 *Nonvolatile Contaminants Specification*—The maximum amount of nonvolatile residue acceptable is 1 mg/g of CO_2 or 1 ppm (w/w).

4.1.6 *Specification Summary*—Proposed minimum specifications for SFE and SFC CO_2 are summarized in Table 1.

5. Gas Handling and Safety

5.1 The safe handling of compressed gases and cryogenic liquids for use in chromatography is the responsibility of every laboratory. The Compressed Gas Association, Inc. (CGA), a member group of specialty and bulk gas suppliers, publishes the following guidelines to assist the laboratory chemist in establishing a safe work environment: CGA P-1, CGA G-5.4, CGA P-9, CGA V-7, CGA P-12, G-6, and HB-3.

6. Representative Analysis Method for Liquid-Phase Contaminants

6.1 Contaminants dissolved in the liquid phase of CO_2 are the most critical to the success of an SFE or SFC experiment. The literature provides a wide variety of analytical methods for detecting liquid-phase trace contaminants, any of which can be used by gas suppliers as long as the method can achieve the detectability and statistical requirements recommended in this guide.

6.2 *Adsorbent Concentration Method*—Outlined below is a representative method for liquid-phase contaminants, referred to as the adsorbent concentration method.

6.2.1 The method is included to develop the quantitation and statistical calculations discussed in Section 8; however, this guide does not mandate its use.

6.2.2 *Apparatus:*

6.2.2.1 *Gas Chromatograph*—The procedure requires a gas chromatograph equipped with both an FID and an ECD. The LLDR[5] for the FID must be 0.25 ng ± 0.1 ng of HD at a signal-to-noise ratio of 3:1. The LLDR for the ECD must be

TABLE 1 Proposed Minimum Specifications for SFE and SFC CO_2

Contaminant	Maximum Single Concentration	Total Concentration
Liquid-phase (SFE)		
FID responsive	1 ppb w/w	10 ppb w/w
ECD responsive	0.2 ppb w/w	2 ppb w/w
Liquid-phase (SFC)		
FID responsive	5 ppb w/w	50 ppb w/w
ECD responsive	1 ppb w/w	10 ppb w/w
Moisture	...	1 ppm m/m
Gas phase		
Oxygen	...	5 ppm m/m
THC	...	5 ppm m/m
Nonvolatile	...	1 ppm w/w