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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 E 1449 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 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 the 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 2504 Test Method for Noncondensable Gases in C_3 and Lighter Hydrocarbon Products by Gas Chromatography[2]

D 2820 Test Method for C Through C_5 Hydrocarbons in the Atmosphere By Gas Chromatography[3]

D 3670 Guide for Determination of Precision and Bias of Methods of Committee D-22[4]

D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)[4]

D 3687 Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Methods[4]

D 4178 Practice for Calibrating Moisture Analyzers[5]

D 4532 Test Method for Respirable Dust in Workplace Atmosphere[4]

E 260 Practice for Packed Column Gas Chromatography[6]

E 355 Practice for Gas Chromatography Terms and Relationships[6]

E 594 Practice for Testing Flame Ionization Detectors Used in Gas Chromatography[6]

E 697 Practice for Use of Electron-Capture Detectors in Gas Chromatography[6]

E 1449 Guide for Supercritical Fluid Chromatography Terms and Relationships[6]

E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs[6]

2.2 *CGA Publications:*[7]

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

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Discontinued*—See 1992 *Annual Book of ASTM Standards*, Vol 05.01.

[4] *Annual Book of ASTM Standards*, Vol 11.03.

[5] *Annual Book of ASTM Standards*, Vol 05.02.

[6] *Annual Book of ASTM Standards*, Vol 14.02.

[7] Available from Compressed Gas Association, Inc., 1725 Jefferson Davis Highway, Arlington, VA 22202-4100.

CGA P-1 Safe Handling of Compressed Gases in Containers
CGA V-7 Standard for Hydrogen Piping Systems at Consumer Locations
CGA P-9 The Inert Gases: Argon, Nitrogen and Helium
CGA V-7 Standard Method of Determining Cylinder Valve Outlets Connections for Industrial Gas Mixtures
CGA P12 Safe Handling of Cryogenic Liquids
G6 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)[8] 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 E 355). 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.

4.1.1.4 When specifying an FID response for SFC, the generally accepted LLDR for a FID is 0.25 ± 0.1 ng for a single component with a signal-to-noise ratio of 3:1. Therefore, "20" $\times$ 0.25 ng = 5 ng to the detector (one peak), and "200" $\times$ 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 E 594).

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

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 E 697).

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.

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

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 V-7, CGA P-9, CGA V-7, CGA P12, G6, 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[8] 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 0.05 ng ± 0.02 ng HCB. The detectors are joined to the column using a "Y" separator and are back-pressure split at a 10:1 FID-ECD ratio (see Practices E 260 and E 1510).

(1) Also, the gas chromatograph must be equipped to accommodate an external thermal desorption and cryofocusing unit, and it must be configured for wide-bore, open-tubular columns and temperature programming up to 270°C.

(2) Any common detector recording device may be used, such as a computerized GC data system or an integrator.

6.2.2.2 *Gas Chromatography Column*—A wide-bore (0.53-mm), open-tubular, fused-silica column 30 m in length is used for this method. The column is coated with a non-polar, polysiloxane stationary phase (100 % dimethyl or 95 % dimethyl), at a film thickness of 1.0 µm.

6.2.2.3 *Thermal Desorption/Cryofocusing Unit*—An apparatus capable of thermally desorbing glass Tenax TA cartridges up to 300°C is required. Also, the unit must be able to cryogenically focus the desorbed output on or near the head of the GC column, and it must be equipped to support the Tenax TA cartridge during the vaporization of liquid-phase CO_2.

6.2.2.4 *Capillary Restrictor*—A fused-silica or metal capillary restrictor is used to vaporize CO_2 from the liquid phase of the cylinder. The restrictor is calibrated to regulate the CO_2 liquid flow at a rate between 1 and 2 g/min.

6.2.3 *Reagents and Materials*:

6.2.3.1 HD ($C_{16}H_{34}$) is used as the representative internal standard for the FID, and HCB (C_6Cl_6) is used as the standard for the ECD. Pure materials must be purchased with at least 99 % purity.

6.2.3.2 "Spectrophotometric" or "HPLC" grades of hexane are required to prepare internal standard solutions.

6.2.3.3 Solutions containing both of the internal standards are prepared gravimetrically in high-purity hexane. The standard solutions are prepared so that a small volume (for example, 0.5 µL) injected onto the Tenax TA adsorbent cartridge will deposit a mass of each the internal standards equivalent to the reportable contaminant level for the mass of CO_2 collected.

6.2.4 *Procedure*:

6.2.4.1 Fit the calibrated capillary restrictor to the outlet of the SFE CO_2 cylinder. Then seal the tip of the restrictor into the apparatus holding the Tenax TA cartridge, allow the CO_2 to decompress, and vaporize from the cylinder directly onto the cartridge holding 1 g of Tenax TA. The mass of liquid CO_2 vaporized, generally 5 to 50 g, will be appropriate for the grade and purity of CO_2 to be certified. The temperature of the adsorbent cartridge will approach −50°C during vaporization; it need not be controlled.

6.2.4.2 After the CO_2 is vaporized, inject a small volume (0.5 to 1.0 µL) of the internal standard solution containing HD and HCB into the adsorbent cartridge. The quantity of standard injected should deposit approximately 2 ng of HD and approximately 0.4 ng of HCB per g of CO_2 vaporized. The quantity of standard injected must yield a readily detectable signal for each of the internal standards on their respective detectors. For higher-purity CO_2 materials, the quantities of the internal standards deposited must be reduced correspondingly.

6.2.4.3 Next, heat the adsorbent tube ballistically (>300°C/min) to desorb the volatile contaminants thermally. The desorbed contaminants will be cryogenically collected at or near the head of the GC column. The chromatogram is produced by temperature programming the gas chromatograph from 50 to 270°C at 20°/min. Pass the column effluent through a "Y" separator, and route the flow to each of the detectors through deactivated fused-silica tubing. Finally, regulate the detector flows at a 10:1 (FID:ECD) ratio using back-pressure control, and record the detector signals using the selected recording device.

7. Analysis Methods for Other Contaminants

7.1 *Moisture*—The maximum amount of moisture is 1 ppm (mole or volume basis). Measurements are to be made from the material volatilized from the CO_2 liquid phase. Any common instrumental method suitable for measuring moisture in the presence of liquid phase CO_2 may be used (see Practice D 4178).

7.2 *Analysis of Gas-Phase Contaminants*:

7.2.1 *Oxygen (or Oxygen/Argon)*—The maximum amount of oxygen (or unresolved oxygen/argon) is 5 ppm (mole or volume basis). Measure the material volatilized from the CO_2 liquid phase. This guide uses a gas chromatograph for the analysis, but any other analyzer suitable for detecting oxygen in the presence of CO_2 can be used. Calibrate the instrument selected for the analysis with a suitable gas reference standard and appropriate techniques (see Test Method D 2504).

7.2.2 *Gas-Phase Total Hydrocarbons*—The maximum amount of total gas-phase hydrocarbons is 5 ppm (mole or volume basis). Analysis can be made on the material volatilized from the CO_2 liquid phase. This guide uses an FID-type total hydrocarbon analyzer for the analysis, calibrated with a suitable gas reference standard of methane or propane. The total gas-phase hydrocarbon concentration is expressed in terms of the equivalent methane or propane concentration (see Test Method D 2820).

7.3 *Nonvolatile Contaminants*—The maximum amount of nonvolatile residue is 1 mg/g of CO_2 or 1 ppm w/w. Using a capillary restrictor similar to that used for the liquid-phase contaminant analysis, volatilize approximately 100 g of liquid-phase CO_2 into a suitable small, pretreated weighing vessel. Heat the residue left in the vessel to 250°C for 30 min to evaporate the volatile liquid-phase contaminants. Then determine the mass of the residue, and report the concentration of the nonvolatile contaminants on a mass basis relative to the mass of CO_2 volatilized (see Test Method D 4532).

8. Results

8.1 *Calculation (See Guide D 3670)*:

8.1.1 *Liquid-Phase Contaminants*:

8.1.1.1 Although not rigorously true, the response factor of each of the internal standards is assumed to be the same as the impurities of interest or "1" on the respective detectors over the concentration range of 0.005 to 50 ng.

8.1.1.2 From the FID peak area report of the recording device, locate the area of the signal from the HD internal standard (S_{hd}). Then calculate the response factor (RF_{hd}) for HD on a mass basis by dividing the peak area (S_{hd}) by the known mass of HD (M_{hd}) deposited. For each contaminant (i ... n) peak reported, divide the area of the peak (S_i) by the response factor for HD (RF_{hd}) to determine the equivalent mass of each contaminant (EM_i) in terms of HD. Divide the total area reported for the chromatogram (S_t) by the response factor for HD (RF_{hd}) to determine the equivalent mass of all contaminants (EM_t) present. That is:

$$RF_{hd} = \frac{S_{hd}}{M_{hd}} \tag{1}$$

$$\sum_{i}^{n} EM_{\mathrm{i-n}} = \frac{S_{\mathrm{i-n}}}{RF_{\mathrm{hd}}} \tag{2}$$

and

$$EM_t = \frac{S_t}{RF_{hd}} \tag{3}$$

8.1.1.3 For each peak reported, divide each of the calculated EM_i by the mass of CO_2 volatilized to determine the relative equivalent contaminant concentration (C_i). For the total chromatogram, divide the calculated EM_t by the mass of CO_2 volatilized to determine the total relative equivalent contaminant concentration (C_t). That is:

$$C_i = \frac{EM_i}{(CO_2)_m} \tag{4}$$

$$C_t = \frac{EM_t}{(CO_2)_m} \tag{5}$$

where:

$(CO_2)_m$ = the mass of carbon dioxide.

8.1.1.4 The CO_2 material meets the minimum purity specifications for FID/SFE applications if no single C_i is greater than 1 ppb w/w and C_t is no greater than 10 ppb w/w.

8.1.1.5 Repeat the calculation procedure for the peak area report from the ECD detector. The same calculation algorithm applies, except that the subscripts referring to the internal standard change from HD to HCB. The CO_2 material meets the minimum purity specifications for ECD SFE applications if no single C_i is greater than 0.2 ppb w/w and C_t is no greater than 2 ppb w/w.

8.1.2 *Other Contaminants*—No special calculations are required for the other contaminants. Concentrations are reported as discussed above.

8.2 *Statistics*:

8.2.1 This guide recommends that the method selected for certification of CO_2 meet certain statistical requirements. The performance criteria below assume a single laboratory and a single operator; no criteria are set for multiple operator repeatability or interlaboratory correlation. Guide D 3670 may be used to define the precision and experimental bias. A recommended guideline to follow for statistical analysis is *Detection in Analytical Chemistry Importance, Theory and Practice*.[9]

8.2.2 *Blank Runs*:

8.2.2.1 The gas supplier must run blank samples before each certification run to demonstrate the validity of the certification method. For the representative method discussed above, a blank sample is defined as thermal desorption of a clean, undeposited Tenax TA cartridge containing no internal standard. The blank thermal desorption is then followed by cryofocusing and temperature-programmed GC analysis in the normal manner.

8.2.2.2 The chromatogram from the blank run should contain no peaks greater than one-tenth (10 %) of the detectability criteria for the intended grade of CO_2 material to be certified. For example, the detectability criteria for standard grade SFE CO_2 on the FID detector are 1 ppb w/w for a single peak and a total of 10 ppb w/w for all peaks. The blank run preceding analysis of this grade of material must indicate no single peak greater than 0.1 ppb w/w and a total of no more than 1 ppb w/w for all peaks.

8.2.3 *Internal Standard Repeatability*:

8.2.3.1 The gas supplier must demonstrate that the analysis is repeatable on each detector before offering for sale any product claiming conformance to this guide. Periodically thereafter, the gas supplier must make triplicate runs of the responses for the internal standards. For the representative method discussed above, this test is accomplished by loading a clean, undeposited Tenax TA cartridge with a typical quantity of internal standard solution only (no CO_2). Tenax-TA may be cleaned by washing with 10 volume of pesticide grade hexane and drying carefully under a positive flow of ultra high-purity nitrogen for 15 min. The cartridge is thermally desorbed, and the remainder of the analysis is performed in the normal manner. Subsequent independent samples are run the same way (see Practices D 3686 and D 3687).

8.2.3.2 On the FID detector, the coefficient of variation for hexadecane (CV_{hd}) is calculated by dividing the standard deviation of the set of three (or more) peak areas by the mean of the peak area responses. On the ECD detector, the calculation is repeated for the hexachlorobenzene standard (CV_{hcb}).

8.2.3.3 To meet the repeatability criteria of this guide, both CV_{hd} and CV_{hcb} must not exceed 10 %.

8.2.3.4 The gas supplier must also demonstrate that the product analysis is repeatable on each detector. Prior to selling any product claiming conformance to this guide, and periodically (no less than once every 90 days) thereafter, the gas supplier must make triplicate runs of randomly selected production CO_2 cylinders. For the representative method discussed above, this test is accomplished by performing the entire analysis, CO_2 volatilization and internal standard loading, in the normal manner. The same cylinder of CO_2 is analyzed at least three times the same way. Data and results are to be maintained for at least one year, from the date of analysis, for review.

8.2.3.5 On the FID detector, the coefficient of variation for FID-responsive contaminants (CV_{FID}) is calculated by dividing the standard deviation of the set of three (or more) total peak areas by the mean of the total peak area responses. The response from the internal standard is subtracted from the total area for this calculation. On the ECD detector, the calculation is repeated for the ECD-responsive contaminants, yielding CV_{ECD}.

8.2.4 *CO_2 Sample Repeatability*—To meet the repeatability criteria of this guide, both CV_{FID} and CV_{ECD} must not exceed 25 % or three sigma based on experimental error analysis.

9. Report

9.1 Purchasers of CO_2 for SFE applications may request verification of certification. In addition, gas suppliers may want to promote the quality of their CO_2 products by claiming conformance to this guide.

9.2 *Certificate of Analysis*—Gas suppliers may claim conformance to this guide by providing the following information on the certificate of analysis:

(1) Company name, address, and phone;

(2) Customer name, address, item number, and P.O. Box number;

(3) Certification date;

(4) Analyst signature;

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[9] Curie, L. A., *Detection in Analytical Chemistry Importance, Theory and Practice*, ACS Symposium Series 361, American Chemical Society, Washington, DC, 1988.

(5) Approver signature;

(6) Cylinder number or bar code assigned to cylinder;

(7) Analytical method for liquid-phase contaminants; and

(8) Analytical data (actual analytical values to be provided):

Contaminants	Maximum Single Concentration	Total Concentration
Liquid-phase contaminants		
FID-responsive	C_i ppb w/w	C_t ppb w/w
ECD-responsive	C_i ppb w/w	C_t ppb w/w
Moisture		C_{H2O} ppm m/m
Gas-phase contaminants		
Oxygen	...	O_2 ppm m/m
THC	...	C_{thc} ppm m/m
Nonvolatile contaminants	...	C_{nv} ppm w/w

9.2.1 *Administrative Information*—This product was analyzed in accordance with and meets the purity specifications defined in Guide E 1747.

9.2.2 *Technical Data*—Gas suppliers may also make use of the provisions of this guide on the cylinder label:

(1) Company name, address, and phone;

(2) Customer name, address, item number, and P.O. Box number;

(3) Certification date;

(4) Cylinder number or bar code assigned to cylinder; and

(5) Analytical data (actual analytical values to be provided):

Contaminant	Maximum Single Concentration	Total Concentration
Liquid-phase contaminants		
FID-responsive	C_i ppb w/w	C_t ppb w/w
ECD-responsive	C_i ppb w/w	C_t ppb w/w
Moisture		C_{H2O} ppm m/m
Gas-phase contaminants		
Oxygen	...	O_2 ppm m/m
THC	...	C_{thc} ppm m/m
Nonvolatile contaminants	...	C_{nv} ppm w/w

9.2.3 *Conformance Statement*—Meets Guide E 1747.

9.2.4 *Liquid-Phase Contaminant Analysis Only*—Certain customers may have no interest in contaminants other than those in the liquid phase. The gas supplier may elect not to perform (or to perform but not to document) analysis of the moisture, gas-phase contaminants, and nonvolatile contaminants. If this decision is made, the certificate of analysis and label information must be modified to exclude the analyses not performed. The ASTM standard conformance statements must also be modified to include the phrase "for liquid-phase contaminants only."

9.2.5 *Supplied Chromatogram*—Certain SFE or SFC CO_2 purchasers may wish to have a copy of the actual chromatograms from the FID or ECD detectors, or both. Gas suppliers may provide these at their option.

9.2.5.1 To comply with the recommendations of this guide, the GC temperature programming should be superimposed on the retention time axis on the chromatogram to indicate the retention time at which a certain temperature was achieved. This provision assists the SFE or SFC practitioner in determining the approximate boiling point of contaminants.

10. Keywords

10.1 fluid purity; supercritical carbon dioxide; supercritical fluid chromatography; supercritical fluid extraction