

Definitions of VOC and ROG

Last Revised November 2004

1. U.S. EPA Definition of VOC (Volatile Organic Compounds):

The U.S. Environmental Protection Agency (U.S. EPA) defines and uses the term Volatile Organic Compounds (VOC). The term VOC is defined in the Federal Register. The original definition of VOC made reference to the vapor pressure of the compounds (greater than 0.1 millimeter of mercury) as a determinant of volatility. However, the current definition relies solely on a list of exempted compounds having "negligible photochemical reactivity".

U.S. EPA periodically exempts additional compounds. A number of proposed exemptions are pending. A summary of petitions and rulemakings follows.

FINAL RULEMAKINGS AND OTHER ACTIONS:

- U.S. EPA exempted **t-Butyl Acetate**, with *special provisions*, which are detailed below, in response to petition from ARCO Chemical Company [now Lyondell] (submitted 1/17/97, proposed September 30, 1999, see 64 FR 52731); published in the Federal Register, November 29, 2004 (69 FR 69298), effective December 29, 2004.

The Federal Register says: "This revision modifies the definition of VOC to say that t-butyl acetate (also known as tertiary butyl acetate or informally as TBAC or TBAc) will not be VOC for purposes of VOC emissions limitations or VOC content requirements, but will continue to be VOC for purposes of all recordkeeping, emissions reporting, and inventory requirements which apply to VOC."

- U.S. EPA exempted 4 compounds, including 3 HFE/HFC compounds and methyl formate, as detailed below; published in the Federal Register, November 29, 2004 (69 FR 69290), effective December 29, 2004.

In the same action, U.S. EPA also added nomenclature designations of "HFE-7100" and "HFE-7200" to two previously exempted compounds.

The four exempted compounds are:

- ❖ 1,1,1,2,2,3,3-heptafluoro-3-methoxy-propane ($n\text{-C}_3\text{F}_7\text{OCH}_3$) (also known as **HFE-7000**) – petition from 3M Performance Chemicals and Fluids Division (submitted February 5, 1999) [*Proposed September 3, 2003, see 68 FR 52373*]
- ❖ 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-(trifluoromethyl) hexane (also known as **HFE-7500**, **HFE-s702**, **T-7145**, or **L-15381**) – petition from 3M Corporation, St. Paul, MN (submitted August 21, 2000). [*Proposed September 3, 2003, see 68 FR 52373*]
- ❖ 1,1,1,2,3,3,3-heptafluoropropane (known as **HFC-227ea**) – petition from Great Lakes Chemical Corporation (submitted February 18, 1998) [*Proposed September 3, 2003, see 68 FR 52373*]
- ❖ **Methyl Formate** – petition from Foam Supplies, Inc., Earth City, Missouri (submitted February 12, 2002). [*Proposed September 3, 2003, see 68 FR 52373*]
- U.S. EPA exempted **Methyl acetate**, in response to petition from Eastman Chemical, April 9, 1998 (63 FR 17331), effective May 11, 1998.
- The Alliance for Responsible Atmospheric Policy, Arlington, Virginia, petitioned to exempt 22 compounds, primarily **HFCs and HCFCs**, but later withdrew five of these. U.S. EPA exempted 16 of the 17 requested compounds (excluding HCFC-150a). The final rule was published August 25, 1997 (62 FR 44900), effective September 24, 1997.
- In response to petitions, the U.S. EPA exempted **HFC 43-10mee**, **HCFC 225ca**, and **HCFC 225cb**. The final rule was published October 8, 1996 (61 FR 52848), and became effective November 7, 1996.
- **Perchloroethylene** was exempted by final rule published February 7, 1996 (61 FR 4588).
- **Acetone** was exempted by final rule published June 16, 1995 (60 FR 31633).

- U.S. EPA, OAQPS, held a workshop to evaluate aspects of its reactivity policy, such as a molar vs. gram basis for reactivity. The national workshop took place May 12-14, 1998 in North Carolina, and a Reactivity Research Working Group was formed to foster a public/private partnership to sponsor and guide scientific research regarding ozone reactivity.

PENDING RULEMAKINGS AND PETITIONS (as of November 30, 2004):

- Below is the list of Compounds for which U.S. EPA has Received Petitions Requesting VOC Exempt Status and for which U.S. EPA has Published no Final Action (as of November 30, 2004):
 1. **1-Bromopropane** (also known as **n-propyl bromide**) - submitted by Enviro Tech International, Alameda, CA (submitted 5/10/96). Petition also submitted by Albemarle Corp., Baton Rouge, LA (submitted November 18, 1997)
 2. **Methyl Bromide** - Chemical Manufacturers Association, Washington, DC (submitted (7/19/96)
 3. **n-Alkanes (C₁₂ - C₁₈)** - The Aluminum Association, Washington, DC (submitted 11/27/96)
 4. **Technical white oils** - The Printing Industries of America and Pennzoil Products Company (submitted 12/20/96)
 5. **Benzotrifluoride** - Occidental Chemical Company, Niagara Falls, NY (submitted 3/11/97). Also Kowa America Corp., New York, NY (submitted 7/29/02).
 6. **Carbonyl Sulfide (COS)** - E.I. du Pont de Nemours and Company (submitted 8/11/97). Petition also submitted by Texas Mid-Continent Oil & Gas Association (submitted December 5, 1997)
 7. **trans-1,2-dichloroethylene** - 3M Corporation, St. Paul, MN (submitted October 8, 1997)
 8. **Dimethyl succinate** - Dibasic Esters Group, affiliated with the Synthetic Organic Chemical Manufacturers Association, Inc. (submitted October 14, 1997)
 9. **Dimethyl glutarate** - Dibasic Esters Group, affiliated with the Synthetic Organic Chemical Manufacturers Association, Inc. (submitted October 14, 1997). Submitted in the same petition as for dimethyl succinate.
 10. **Carbon Disulfide** - Texas Mid-Continent Oil & Gas Association, (submitted December 5, 1997)
 11. **Acetonitrile** - BP Chemicals and GNI Chemicals Corporation, (submitted January 21, 1998)
 12. **Toluene Diisocyanate (TDI)** - Chemical Manufacturers Association [The Diisocyanate Panel of CMA reported the following members: ARCO Chemical Company, BASF Corporation, Bayer Corporation, The Dow Chemical Company, and ICI Americas, Inc.] (submitted January 22, 1998)
 13. **Methylene Diphenyl Diisocyanate (MDI)** - Chemical Manufacturers Association [The Diisocyanate Panel of CMA reported the following members: BASF Corporation, Bayer Corporation, The Dow Chemical Company, ICI Americas, Inc., and Lyondell Chemical Company], (submitted August 19, 1998)
 14. **Propylene carbonate** - Huntsman Corporation, Austin, Texas (July 27, 1999)
 15. **Methyl pivalate** - Exxon Chemical Company, Houston, TX (November 22, 1999)

The complete federal definition and the list of exempted compounds to date are shown on the following page.

U.S. EPA Definition of VOC (effective as of December 29, 2004): (based on final rules to date)

40 CFR Part 51 Section 51.100 Definitions.

(s) **Volatile organic compounds (VOC)** means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.

(1) This includes any such organic compound other than the following, which have been determined to have negligible photochemical reactivity:

methane;	[74-82-8] *
ethane;	[74-84-0]
methylene chloride (dichloromethane);	[75-09-2]
1,1,1-trichloroethane (methyl chloroform);	[71-55-6]
1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113);	[76-13-1]
trichlorofluoromethane (CFC-11);	[75-69-4]
dichlorodifluoromethane (CFC-12);	[75-71-8]
chlorodifluoromethane (HCFC-22);	[75-45-6]
trifluoromethane (HFC-23);	[75-46-7]
1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114);	[76-14-2]
chloropentafluoroethane (CFC-115);	[76-15-3]
1,1,1-trifluoro-2,2-dichloroethane (HCFC-123);	[306-83-2]
1,1,1,2-tetrafluoroethane (HFC-134a);	[811-97-2]
1,1-dichloro-1-fluoroethane (HCFC-141b);	[1717-00-6]
1-chloro-1,1-difluoroethane (HCFC-142b);	[75-68-3]
2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124);	[2837-89-0]
pentafluoroethane (HFC-125);	[354-33-6]
1,1,2,2-tetrafluoroethane (HFC-134);	[359-35-3]
1,1,1-trifluoroethane (HFC-143a);	[420-46-2]
1,1-difluoroethane (HFC-152a);	[75-37-6]
parachlorobenzotrifluoride (PCBTF);	[98-56-6]
cyclic, branched, or linear completely methylated siloxanes;	[various]
acetone;	[67-64-1]
perchloroethylene (tetrachloroethylene);	[127-18-4]
3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca);	[422-56-0]
1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb);	[507-55-1]
1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC-43-10mee);	[138495-42-8]
difluoromethane (HFC-32);	[75-10-5]
ethylfluoride (HFC-161);	[353-36-6]
1,1,1,3,3,3-hexafluoropropane (HFC-236fa);	[690-39-1]
1,1,2,2,3-pentafluoropropane (HFC-245ca);	[679-86-7]
1,1,2,3,3-pentafluoropropane (HFC-245ea);	[24270-66-4]
1,1,1,2,3-pentafluoropropane (HFC-245eb);	[431-31-2]
1,1,1,3,3-pentafluoropropane (HFC-245fa);	[460-73-1]
1,1,1,2,3,3-hexafluoropropane (HFC-236ea);	[431-63-0]
1,1,1,3,3-pentafluorobutane (HFC-365mfc);	[406-58-6]
chlorofluoromethane (HCFC-31);	[593-70-4]
1-chloro-1-fluoroethane (HCFC-151a);	[1615-75-4]
1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a);	[354-23-4]
1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane (C ₄ F ₉ OCH ₃ or HFE-7100);	[163702-07-6]
2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane ((CF ₃) ₂ CF ₂ OCH ₃);	[163702-08-7]
1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane (C ₄ F ₉ OC ₂ H ₅ or HFE-7200);	[163702-05-4]
2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane ((CF ₃) ₂ CF ₂ OC ₂ H ₅);	[163702-06-5]
methyl acetate,	[79-20-9]
1,1,1,2,2,3,3-heptafluoro-3-methoxy-propane (n-C ₃ F ₇ OCH ₃ , HFE-7000)	[]
3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-(trifluoromethyl) hexane (HFE-7500)	[]
1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea)	[431-89-0]
methyl formate (HCOOCH ₃),	[107-31-3]

and perfluorocarbon compounds which fall into these classes: [various]

- (I) Cyclic, branched, or linear, completely fluorinated alkanes;
- (ii) Cyclic, branched, or linear, completely fluorinated ethers with no unsaturations;
- (iii) Cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturations; and
- (iv) Sulfur containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine.

(2) For purposes of determining compliance with emissions limits, VOC will be measured by the test methods in the approved State implementation plan (SIP) or 40 CFR Part 60, Appendix A, as applicable. Where such a method also measures compounds with negligible photochemical reactivity, these negligibly-reactive compounds may be excluded as VOC if the amount of such compounds is accurately quantified, and such exclusion is approved by the enforcement authority.

(3) As a precondition to excluding these compounds as VOC or at any time thereafter, the enforcement authority may require an owner or operator to provide monitoring or testing methods and results demonstrating, to the satisfaction of the enforcement authority, the amount of negligibly-reactive compounds in the source's emissions.

(4) For purposes of Federal enforcement for a specific source, the EPA shall use the test methods specified in the applicable EPA-approved SIP, in a permit issued pursuant to a program approved or promulgated under Title V of the Act, or under 40 CFR Part 51, Subpart I or Appendix S, or under 40 CFR Parts 52 or 60. The EPA shall not be bound by any State determination as to appropriate methods for testing or monitoring negligibly-reactive compounds if such determination is not reflected in any of the above provisions.

(5) The following compound(s) are VOC for purposes of all recordkeeping, emissions reporting, photochemical dispersion modeling and inventory requirements which apply to VOC and shall be uniquely identified in emission reports, but are not VOC for purposes of VOC emissions limitations or VOC content requirements:

t-butyl acetate

[540-88-5]

-
- NOTE: Chemical Abstract Service (CAS) identification numbers have been included in brackets [] after the compounds for convenience.

2. California Air Resources Board's Definition of ROG (Reactive Organic Gases):

The California Air Resources Board's (ARB's) Emission Inventory Branch (EIB) uses the terms Total Organic Gases (TOG) and Reactive Organic Gases (ROG). California air pollution control districts report Total Organic Gases (TOG) to the Air Resources Board's emission inventory.

For each source category, the ARB derives a value for the Reactive Organic Gases (ROG) by multiplying the reported TOG by the Fraction of Reactive Organic Gases (FROG). Each source category is keyed to one of several hundred available chemical speciation profiles. For each category, the FROG value is calculated as the weight fraction of those species designated by the ARB as reactive in the speciation profile applicable to the category. The ARB's organic gas speciation profiles are available for download from the ARB's web site at <http://www.arb.ca.gov> or specifically at <http://www.arb.ca.gov/ei/speciate/speciate.htm>.

The relationships among these organic gas terms are summarized as follows:

$$\begin{array}{l} \text{TOG} \\ \text{(Total Organic Gas)} \end{array} - \begin{array}{l} \text{Exempt cmpds} \\ \text{[ARB list of methane,} \\ \text{CFCs, etc.]} \end{array} = \begin{array}{l} \text{ROG} \\ \text{(Reactive Organic Gas)} \end{array}$$

$$\begin{array}{l} \text{TOG} \\ \text{(Total Organic Gas)} \end{array} \times \begin{array}{l} \text{FROG} \\ \text{(Fraction of Reactive} \\ \text{Organic Gas)} \end{array} = \begin{array}{l} \text{ROG} \\ \text{(Reactive Organic Gas)} \end{array}$$

Background Regarding Federal vs. State Exempt List: The original "Air Pollution Emission Inventory Program" manual, ARB, March 1982, listed the compounds which the ARB initially treated as exempted from ROG. The list differed somewhat from the U.S. EPA's list of exempted VOCs even at the time, in that ARB's definition of ROG did not exempt Ethane. As discussed in the prior section, U.S. EPA later exempted additional compounds from the federal definition of VOC as well.

Subsequently, the Air Resources Board was petitioned regarding exemptions from the ARB's regulations. The ARB staff formed a Reactive Organic Gas Technical Committee (ROGTC), made up of staff from the ARB's affected divisions and district representatives, to systematically evaluate the proposed exemption of these compounds. At a public hearing in September 1995, the Air Resources Board took action to revise the definition of "Volatile Organic Compounds" that is used in the consumer products regulations, based on the recommendations of the ROGTC. Methyl siloxanes were added to the list of exempted compounds, and parachlorobenzotrifluoride, acetone, and ethane were added to the list of exempted compounds with the qualifier that they are "low-reactive organic compounds which have been exempted by the U.S. EPA". Based on the ROGTC's analysis, the staff similarly modified the overall inventory definition of ROG to extend the Board's action on the consumer products regulation "VOC" definition to "ROG" for all inventory applications.

The Air Resources Board exempted Perchloroethylene from the definition of VOC in the consumer products regulations in November 1996. In response to industry petition, the Air Resources Board approved the exemption of Methyl acetate from the definition of VOC in the ARB's regulations for aerosol coatings, consumer products, and antiperspirants and deodorants at a public hearing on November 19, 1998.

As noted above, the ARB's list of compounds has two parts, including a second group of "low-reactive organic compounds which have been exempted by the U.S. EPA". This designation is used for compounds that are expected to have low, but not insignificant, ozone formation impacts in the near-term; however, their future new uses and emissions need to be tracked, and the exemption revisited, if necessary, to ensure there is no future degradation of air quality resulting from increased usage.

Likewise, some compounds that have been exempted from the definition of ROG or VOC may have other adverse impacts, such as toxicity, stratospheric ozone depletion potential, or greenhouse gas potential, that must be considered. Therefore, "exemption" from the definition of ROG or VOC is not an automatic endorsement for increased usage of a compound.

The complete definitions and the list of exempted compounds to date are shown on the following page

ARB's Definitions of TOG and ROG (as of November 2004):

Total Organic Gases (TOG) means compounds of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate.

Reactive Organic Gases (ROG) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, and excluding the following:

	<u>CAS</u> *	<u>(TAC)</u> **
(1) methane;	[74-82-8]	
methylene chloride (dichloromethane);	[75-09-2]	TAC
1,1,1-trichloroethane (methyl chloroform);	[71-55-6]	TAC
trichlorofluoromethane (CFC-11);	[75-69-4]	
dichlorodifluoromethane (CFC-12);	[75-71-8]	
1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113);	[76-13-1]	
1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114);	[76-14-2]	
chloropentafluoroethane (CFC-115);	[76-15-3]	
chlorodifluoromethane (HCFC-22);	[75-45-6]	
1,1,1-trifluoro-2,2-dichloroethane (HCFC-123);	[306-83-2]	
2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124);	[2837-89-0]	
1,1-dichloro-1-fluoroethane (HCFC-141b);	[1717-00-6]	
1-chloro-1,1-difluoroethane (HCFC-142b);	[75-68-3]	
trifluoromethane (HFC-23);	[75-46-7]	
pentafluoroethane (HFC-125);	[354-33-6]	
1,1,2-tetrafluoroethane (HFC-134);	[359-35-3]	
1,1,1,2-tetrafluoroethane (HFC-134a);	[811-97-2]	
1,1,1-trifluoroethane (HFC-143a);	[420-46-2]	
1,1-difluoroethane (HFC-152a);	[75-37-6]	
cyclic, branched, or linear completely methylated siloxanes;	[various]	
the following classes of perfluorocarbons:	[various]	
(A) cyclic, branched, or linear, completely fluorinated alkanes;		
(B) cyclic, branched, or linear, completely fluorinated ethers with no unsaturations;		
(C) cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturations; and		
(D) sulfur-containing perfluorocarbons with no unsaturations and with the sulfur bonds only to carbon and fluorine; and		
(2) the following low-reactive organic compounds which have been exempted by the U.S. EPA:		
acetone;	[67-64-1]	
ethane;	[74-84-0]	
methyl acetate;	[79-20-9]	
perchloroethylene; and	[127-18-4]	TAC
parachlorobenzotrifluoride (1-chloro-4-trifluoromethyl benzene).	[98-56-6]	

* NOTE: Chemical Abstract Service (CAS) identification numbers have been included in brackets [] for convenience.

** NOTE: "TAC" indicates compounds that have been identified by the ARB as Toxic Air Contaminants (TAC). Their "exemption" from the definition of ROG or VOC is not an endorsement for their increased usage.

Prepared November 2004 by Beth Schwehr, California Air Resources Board, Planning and Technical Support Division, Emission Inventory Branch, bschwehr@arb.ca.gov.