*Formaldehyde, acetaldehyde, and acrolein are the three carbonyl compounds that have been identified as adversely affecting human health and are therefore listed in the Toxic Air Contaminant Identification List of California as Category IIa compounds. The U.S. Environmental Protection Agency (EPA) has classified the first two as probable human carcinogens. [Liu, Yu-Yin et al, 2009, Journal of the Air & Waste management Association]*

## 1.- CARB (California Environmental Protection Agency; Air Resources Board)

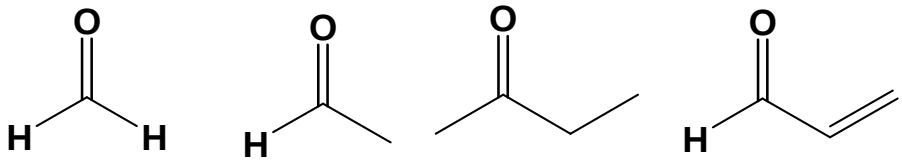
The ARB's toxic air contaminant monitoring programs for hydrocarbon VOCs and Carbonyls are described in:

**Toxic Air Contaminants Monitoring**
**Source: http://www.arb.ca.gov/aaqm/toxics.htm**
**(This page last reviewed July 8, 2010)**

**Definitions:**

**Volatile Organic Compounds -** VOCs are organic compounds that can vaporize easily at ambient temperatures. Some VOCs are highly reactive and play a critical role in the formation of ozone. Other VOCs have adverse, chronic, and acute health effects. In some cases, VOCs can be both highly reactive and potentially toxic. Sources of VOCs include **motor vehicle exhaust,** waste burning, **gasoline marketing**, industrial and consumer products, pesticides, industrial processes, degreasing operations, pharmaceutical manufacturing, and dry cleaning operations.

**Carbonyl Compounds -** Carbonyl compounds (aldehydes and ketones) contain a carbon atom and an oxygen atom linked with a double bond (C=O**). Some carbonyls are highly reactive and play a critical role in the formation of ozone.** Other carbonyls have adverse chronic and acute health effects. In some cases, carbonyls can be both highly reactive and potentially toxic. **The major sources of directly emitted carbonyls are fuel combustion, mobile sources, and process emissions from oil refineries**. To date, the **ARB monitors four carbonyls: formaldehyde, acetaldehyde, methyl ethylketone (MEK), and acrolein.**




**Laboratory analyses of samples are conducted using state-of-the-art techniques.**

- VOC and oxygenated compound samples are collected in stainless steel canisters and are analyzed in the laboratory by two separate gas chromatography (GC) methods for butadiene, aromatic and halogenated, and oxygenated hydrocarbons.

- **Carbonyl compounds** in ambient air samples are collected into adsorbent cartridges and analyzed by high performance liquid chromatography

(HPLC). **(SOP MLD022** - Determination of Carbonyl Compounds in Ambient Air Using High Performance Liquid Chromatography) and

- EPA/625/R-96/-1-b; Compendium Method TP-11A: Determination of Formaldehyde in Ambient Air Using Absorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC)

- **Note that US EPA and CARB agencies have removed acrolein (H-CO-CH=$CH_2$) from the validated list for the measurement using DNPH-cartridge technique, due to its degradation in the presence of the collection media. Other methods have been suggested by other agencies; however none has been validated yet.**

## 2.- Two methods described by Australian Department of Environment, water, Heritage and Arts:

Evaluating the Health Impacts of Ethanol blend Petrol
Final Report KW48A/17/F3.3F (2008)
Appendix B4
Analytical Methodology, Method Proficiency and Speciate list for VOCs determination.
(Downloadable on www.csiro.au)

Speciation of hydrocarbon VOCs, Carbonyl VOCs and minor alcohols (EtOH and MeOH) are outlined in the following sections including:

1. Speciation of hydrocarbon VOCs
    - 57 US EPA/CARB compound priorised for air toxics and photochemical assessmentand additional 41 compounds identified as significant in the VOC emission profile. (C2-C12 anylised by GC-FID)
    - Sampling from CVS dilution tunnel and the evaporative shed into sampling bags prior to transfer to evacuated treated canisters. (Off-line method).

2. Speciation of carbonyl VOCs
    - Eight carbonyl compounds have been reported. These include the three USEPA/CARB PAMS priority compounds for photochemical assessment (formaldehyde, acetaldehyde and acetone) and five additional compounds.

3. Minor alcohols (EtOH and MeOH)
    - Standard methodologies for preparative and instrumental analysis of alcohol compounds were followed with primary reference to the Californian Air Resources Board MLD 101: “procedures for the Analysis of Automotive Exhaust for Methanol and Ethanol”

## 3.- Brasilian regulation for Adehydes in vehicle emissions (In conformity with Resolution CONAMA no. 15/95 & no. 315/02)

**See below emission factor limits for the sum of aldehydes (RCHO). Methodology is based on the same DNPH protocol described before.**

**Tabela 28 – Limites máximos de emissão para veículos leves novos[1]**

| ANO | CO (g/km) | HC (g/km) | NOx (g/km) | RCHO[2] (g/km) | MP[3] (g/km) | EVAP.[4] (g/teste) | CÁRTER | CO-ML (% vol) |
|---|---|---|---|---|---|---|---|---|
| 89 - 91 | 24 | 2,10 | 2,0 | -- | -- | 6 | nula | 3 |
| 92 - 96[6] | 24 | 2,10 | 2,0 | 0,15 | -- | 6 | nula | 3 |
| 92 - 93 | 12 | 1,20 | 1,4 | 0,15 | -- | 6 | nula | 2,5 |
| mar/94 | 12 | 1,20 | 1,4 | 0,15 | 0,05 | 6 | nula | 2,5 |
| jan/97 | 2 | 0,30 | 0,6 | 0,03 | 0,05 | 6 | nula | 0,5 |
| mai/03 | 2 | 0,30 | 0,6 | 0,03 | 0,05 | 2 | nula | 0,5 |
| jan/05 (40%) | 2 | 0,16[5] | 0,25[7] | 0,03 | 0,05 | 2 | nula | 0,5[7] |
| jan/06 (70%) | 2 | ou | ou | 0,03 | 0,05 | 2 | nula | 0,5[7] |
| jan/07 (100%) | 2 | 0,30[6] | 0,60[3] | 0,03 | 0,05 | 2 | nula | 0,5[7] |
| jan/09 | 2 | 0,05[5] ou | 0,12[7] ou | 0,02 | 0,05 | 2 | nula | 0,5[7] |
| jan/09 | 2 | 0,30[6] | 0,25[3] | 0,02 | 0,05 | 2 | nula | 0,5[7] |

1 - Medições de acordo com a NBR6601 (US-FTP75), e conforme as Resoluções CONAMA n° 15/95 e n° 315/02.
2 - Apenas para veículos do ciclo Otto. Aldeídos totais de acordo com a NBR 12026.
3 - Apenas para veículos do ciclo Diesel.
4 - Apenas para veículos do ciclo Otto, exceto a GNV.
5 – Hidrocarbonetos não metano (NMHC).
6 – Hidrocarbonetos totais somente para veículos a GNV, que também atendem ao item (5).
7 – Apenas para veículos do ciclo Otto, inclusive a GNV.