

CASE STUDY: CO₂ quality control for food industries

ChromaS-COS & airmoVOC BTEX



EXPERTS IN GAS ANALYSIS

Updated: November 2013

The problem

CO₂ used in food industries can be produced by two families of processes: natural or chemical. The multiple production possibilities are involving different kind of impurities inside CO₂ (BTEX, Sulfur compounds...).

To help producers to control the quality and purity of Carbon Dioxide, some specialists are proposing limit values for impurities in compliance with health and safety regulations.

- Compressed Gas Association of America (CGA)
www.cganet.com
- International Society of Beverage Technologists (ISBT)
www.bevtech.org
- European Industries Gases Associations (EIGA)
www.eiga.be

One of the most commonly used technologies to control CO₂ quality and purity is Gas Chromatography. Here below are the impurities concentration limits

Compounds	Concentration
Acetaldehyde	0,2 ppm v/v max.
Benzene	0,02 ppm v/v max.
Total Sulfur (TS equivalent S)*	0,1 ppm v/v max.
* if Total Sulfur concentration (TS) is over 0,1 ppm v/v Sulfur, a speciation of each impurity must be done and must be in compliance with the following limits:	
Sulfide Carbonyl (COS)	0,1 ppm v/v max.
Hydrogene Sulfide (H ₂ S)	0,1 ppm v/v max.
Sulfur Dioxide (SO ₂)	1,0 ppm v/v max.

source: CGA/EIGA limiting characteristics commodity specification for carbon dioxide from "carbon dioxide source certification, quality standards and verification", IGC Doc 70/99/E

Sample presentation and specifications

Carbon dioxide is colorless, odorless and is not a fuel gas. It can be found under two phases: liquid or gaseous at temperature between -56.6°C and 31.1°C.

Toxicity

CO₂ is naturally present in ambient air at concentrations changing between 0.03% (300 ppm) and 0.06% (600 ppm), depending on the measurement area. CO₂ becomes hazardous at concentration above 5% volume, or 50,000 ppm) and the limit value (TLV: threshold limit value) or daily maximum exposition limit recommended for an adult is 0.5% (5,000 ppm).

The solution

Chromatotec® proposes its CO₂ analytical system. It is a cabinet including several modules adapted to impurities measurement:

- C51022 – chromaS-COS: module 5U for Total Sulfur analysis: speciation of H₂S, mercaptans, DMS, DMDS, COS, CS₂ and SO₂ is done with FPD Detector (dual Flame Photometric Detector) and a filter specific to sulfur compounds. No quenching with this detector. Computer is included in the 19" rack with Vistachrom software. The software allows:
 - a full control of the complete system
 - a backup and transfer of data
 - traceability of results
 - trend function
- A21022 – airmoVOC BTEX: module 4U for acetaldehyde and BTEX (Benzene, Toluene, Ethylbenzene and Xylenes) analysis with FID Detector (Flame Ionization Detector)
- XXX916 – hydroxychrom: Hydrogen generator module 4U
- XXX031 – airmoPURE-D: zero air generator, 45 psi (3 bar) compressor, VOC filter and air dryer
- XXX901 – airmoPUMP: sampling pump
- XXX043 – installation in a cabinet
- XXX931 – internal calibration module with permeation tube (benzene or Di-Methyl Sulfide)

**>>> airmoVOC BTEX: MCERTS certified (2013) for benzene measurement following EN 14662-3
TÜV certified for BTEX analysis (1996)**



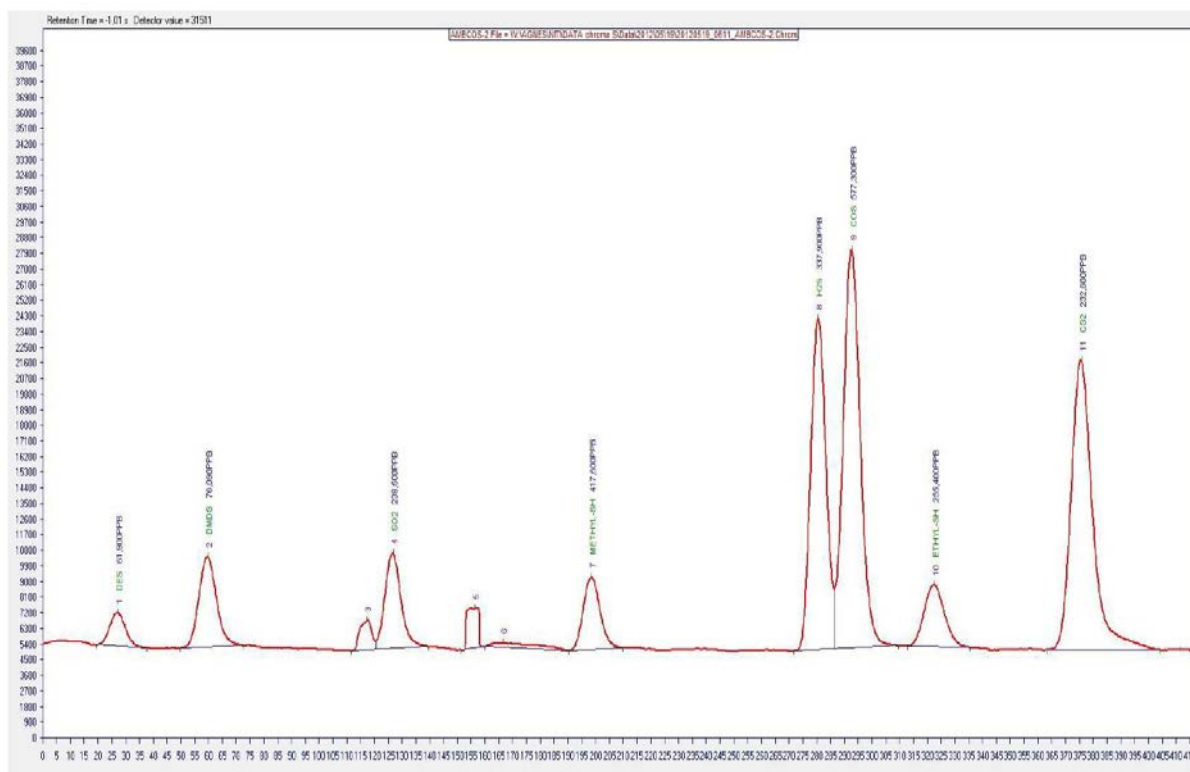
Analytical solution offered by Chromatotec®

Results

Sulfur compounds analysis:

Sulfur analysis (#57960512)	
Cycle time	600 seconds
Amplification	middle (2)
Sampling loop	250 µl
Limit of quantification (H2S)	< 10 ppb

Sample: DES, DMDS, SO₂, Me-SH, H₂S, COS, Et-SH and CS₂



Substance table

Substances						
#	Name	RT Min	RT Max	Select Peak	GC Result formula	With X=
1	DES	16	36	Middle	$0,8 * X^{0,68}$	Area/BS
2	DMDS	50	70	Middle	$0,48 * X^{0,66}$	Area/BS
3	SO ₂	118	138	Middle	$1,05 * X^{0,66}$	Area/BS
4	METHYL-SH	188	208	Middle	$1,6 * X^{0,65}$	Area/BS
5	H ₂ S	275	290	Middle	$0,36 * X^{0,66}$	Area/BS
6	COS	290	310	Middle	$0,9 * X^{0,65}$	Area/BS
7	ETHYL-SH	312	332	Middle	$1,24 * X^{0,66}$	Area/BS
8	DMS	352	367	Middle	$0,74 * X^{0,78}$	Area/BS
9	CS ₂	367	382	Middle	$0,48 * X^{0,68}$	Area/BS

Substances table information:

Substances table name: RSH-COS Author: CHROMATO-SUD

For the analyzer serial number: #57960512 Analyzer type: chroma S

Curve response of detector: Power

$A * X^P + RstOfs$

With X = $(Area + AreaOfs) / BS$

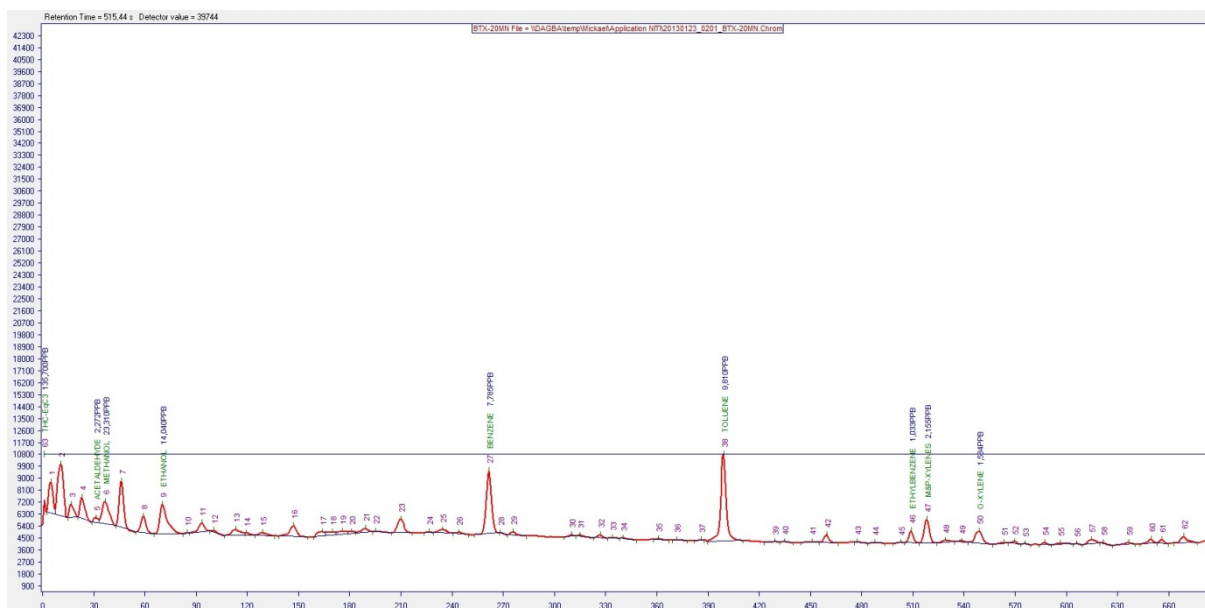
Name	Value
A	0,8
P	0,68
AreaOfs	0
RstOfs	0

Acetaldehyde and BTEX analysis:

Acetaldehyde and BTEX analysis (#28730712)	
Cycle time	1200 seconds
Amplification	high (3)
Trap	3 phases
Limit of quantification (acétaldéhyde)	< 5 ppb

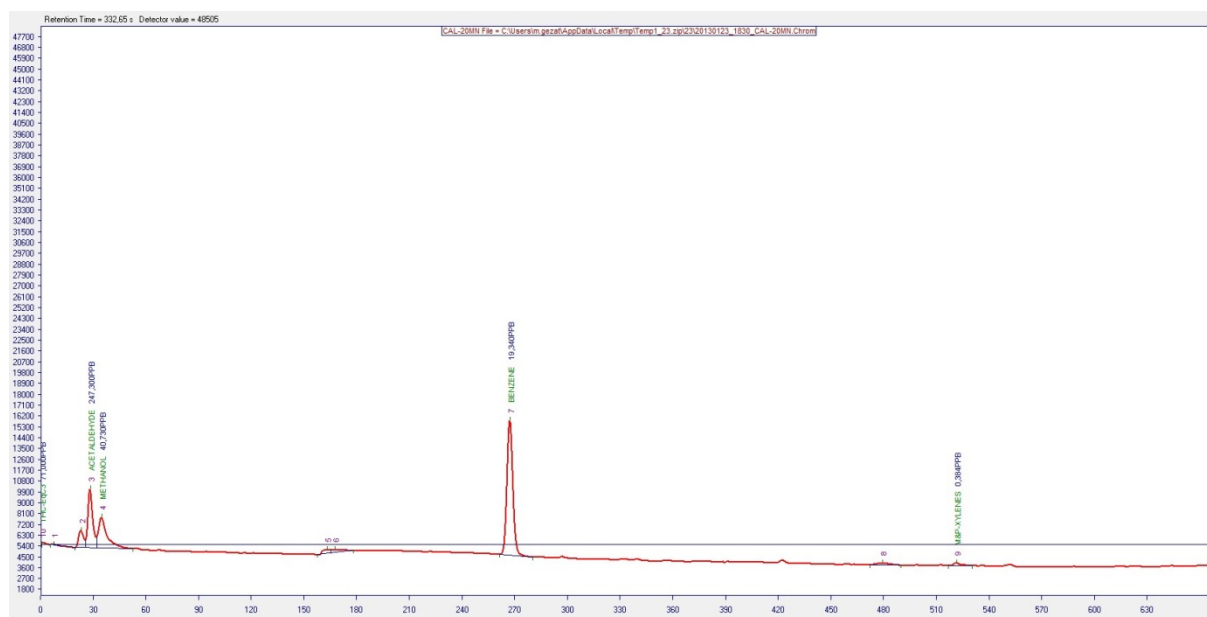
To verify the BS and to validate the results, a benzene permeation tube is used. The permeation tube is installed in a regulated temperature oven placed inside the analyzer. The oven is swept by a constant air or nitrogen flow and delivers a constant gas concentration. Other concentrations are known due to the response factor relating to Benzene.

Chromatogram:



Substance table

Standard chromatogram:



48h continuous analysis of acetaldehyde, standard deviation (Relative Standard Deviation):

< 0,3% over 48H (on retention time)

< 2% over 48H (on concentrations)

Conclusion

To ensure people's safety, CO₂ monitoring is crucial in food industries; Chromatotec® has therefore developed different modules to answer customer needs.

The high stability and the ease of use are making of Chromatotec's analyzers, the perfectly suitable analysis devices for carbon dioxide quality control

To validate and control the stability of the measure, internal calibration systems are used: autoCALIB function is available on the Vistachrom software

Contact : info@chromatotec.com

NORTH AMERICA
CHROMATOTEC Inc.
18333 Egret Bay Blvd, Suite 270,
HOUSTON TX 77058 – USA
Phone: +1 (281) 335 4944
Fax: +1 (281) 335 4943

EUROPE
AIRMOTEC ag SAS
15 rue d'Artiguelongue
F-33240 SAINT-ANTOINE (BORDEAUX)
Tel : +33 (0)557 940 626
Fax : +33 (0)557 940 620

ASIA
CHROMATOTEC Trading (Beijing) Co., Ltd.
Room 1806, Building 1,
Wanda Plaza, No.93, Jianguo Avenue,
Chaoyang District, Beijing 100022, CHINA
Phone & Fax: +86 (0)105 960 3283