

Toxic Organic Compounds of Ambient Air Listed in TO 15 Method

CONTEXT & CHALLENGES

TO 15 is a performance-based method prepared by the United States Environmental Protection Agency (EPA) as a guidance document for monitoring subsets of those Volatile Organic Compounds (VOCs) mentioned in Clean Air Act Amendments of 1990.

This method uses data obtained by GC MS analyzer with spot sampling collection using canister. GC MS needs to work with calibration reference that is not easily obtained on site. This application note describes the results obtained with Chromatotec® GC specific analyzers when monitoring the molecules listed on TO 15.



OUR SOLUTION

Chromatotec® provides its specific airmOZONE analyzer with configuration including following configuration:

- airmoVOC 624 & airmoVOC C₂C₆
- airmoVOC C₂-C₆ & airmoVOC C₆-C₁₂
- airmoVOC C₂-C₆ & airmoVOC C₆-C₁₂ & airmoVOC 624

Configuration is set up according to the specifications: molecules present in ambient air and expected sensitivity.

These analyzers are gas chromatographs equipped with FID detectors (Mass Spectrometry is also available upon request).

Light and heavy VOC compounds can be analyzed by combining chromatographs' configurations.

Separation and sensitivity can be lowered to ppt concentration level by using an embedded trap, a FID detector and H₂ as carrier gas.

The equipment has TUV, mCERTs approval on Benzene. Following determinands have been analyzed: n-hexane, 2,2,4-trimethylpentane, n-heptane, toluene, n-octane, ethyl-benzene, m-xylene and p-xylene, o-xylene, 1,3,5-trimethylbenzene, 1,2,4-Trimethylbenzene, 1,2,3-trimethylbenzene.

Instruments are calibrated with certified primary gas standard using permeation tube which is a major advantage compared to the mass spectrometer. In compliance with EN 14 662-3 (list of the 10 compounds which could potentially interfere with benzene), there is no interference with Benzene.

The analyzer is LINEAR: range 0 / 100 ppb (0/325 µg/m³)(*)

The instruments are fully automated thanks to internal calibration. The VISTACHROM software controls the analyzers and enables storage and display of chromatograms thanks to Peak Viewer.

It is possible to transfer data to a data logger with the following communication protocols: MODBUS RTU, JBUS or German PROTOCOL.

airmoZONE is the solution for in situ VOC analysis.

(*) airmoBTX / airmoVOC C₆-C₁₂, Linearity and repeatability Test available under request)



TARGET MOLECULES

The analyses have been performed with a cylinder containing the following 63 molecules:

No.	Component	Chemical Formula	No.	Component	Chemical Formula
1	Propene	C ₃ H ₆	34	Trichloro Ethylene	C ₂ HCl ₃
2	Dichloro Difluoro Methane	CCL ₂ F ₂ = F12	35	1,2-Dichloro Propane	1,2-C ₃ H ₆ Cl ₂
3	1,1,2,2-Tetrachloro Ethane	C ₂ Cl ₄ = F114	36	Methyl Methacrylate	CH ₂ C(CH ₃)COOCH ₃
4	Chloro Methane	CH ₃ -Cl	37	1,4-Dioxane	C ₄ H ₈ O ₂
5	Vinyl Chloride	C ₂ H ₃ Cl	38	Bromo Di Chloro Methane	CHBrCl ₂
6	1,3-Butadiene	1,3-C ₄ H ₆	39	trans-1,3-Dichloro Propene	trans-1,3-C ₃ H ₄ Cl ₂
7	Bromo Methane	CH ₃ -Br	40	4-Methyl-2-Pentanone = MIBK	C ₄ H ₈ COCH ₃
8	Chloro Ethane	C ₂ H ₅ -Cl	41	Toluene	C ₇ H ₈
9	Trichloro Fluoro Methane	CCL ₃ -F = F11	42	cis-1,3-Dichloro Propene	cis-1,3-C ₃ H ₄ Cl ₂
10	Ethanol	C ₂ H ₅ -OH	43	1,1,2-Trichloro Ethane	1,1,2-C ₂ H ₃ Cl ₃
11	Acrolein	CH ₂ :CHCHO	44	Tetrachloro Ethene	C ₂ Cl ₄ = PER
12	1,1-Dichloro Ethene	1,1-C ₂ H ₂ Cl ₂	45	2-Hexanone = MBK	CH ₃ (CH ₂) ₃ COCH ₃
13	1,1,2-Trichlorotrifluoro Ethane	C ₂ Cl ₃ F ₃ = F113	46	Di Bromo Chloro Methane	CHBr ₂ Cl
14	Acetone	(CH ₃) ₂ CO	47	1,2-Dibromo Ethane	1,2-CH ₂ CH ₂ Br ₂
15	Carbon Disulfide	CS ₂	48	Chlorobenzene	C ₆ H ₅ Cl
16	2-Propanol (IPA)	i-C ₃ H ₇ -OH	49	Ethylbenzene	C ₆ H ₅ C ₂ H ₅
17	Dichloro Methane	CH ₂ Cl ₂	50	p-Xylene	p-C ₆ H ₄ (CH ₃) ₂
18	trans-1,2-Dichloro Ethene	trans-1,2-C ₂ H ₂ Cl ₂	50	m-Xylene	m-C ₆ H ₄ (CH ₃) ₂
19	Methyl-Tert-Butyl Ether (MTBE)	tert-C ₄ H ₉ OCH ₃	51	o-Xylene	o-C ₆ H ₄ (CH ₃) ₂
20	n-Hexane	n-C ₆ H ₁₄ = C6	52	Styrene	C ₆ H ₅ CH=CH ₂
21	1,1-Dichloro Ethane	1,1-C ₂ H ₄ Cl ₂	53	Bromoform	CHBr ₃
22	Vinyl Acetate	CH ₃ COOC ₂ H ₃	54	1,1,2,2-Tetrachloro Ethane	1,1,2,2-C ₂ H ₂ Cl ₄
23	cis-1,2-Dichloro Ethene	cis-1,2-C ₂ H ₂ Cl ₂	55	4-Ethyl Toluene	p-(C ₂ H ₅)C ₆ H ₄ CH ₃
24	Ethyl Acetate	CH ₃ COOC ₂ H ₅	56	1,3,5-Trimethyl Benzene	1,3,5-C ₆ H ₃ (CH ₃) ₃
25	2-Butanone (MEK)	CH ₃ COC ₂ H ₅	57	1,2,4-Trimethyl Benzene	1,2,4-C ₆ H ₃ (CH ₃) ₃
26	Tetrahydrofuran (THF)	(CH ₂) ₄ O	58	1,3-Dichloro Benzene	1,3-C ₆ H ₄ Cl ₂
27	Chloroform	CHCl ₃	59	1,4-Dichloro Benzene	1,4-C ₆ H ₄ Cl ₂
28	1,1,1-Trichloro Ethane	1,1,1-C ₂ H ₃ Cl ₃	60	Benzyl Chloride	C ₆ H ₅ CH ₂ Cl
29	Cyclohexane	(CH ₂) ₆	61	1,2-Dichloro Benzene	1,2-C ₆ H ₄ Cl ₂
30	Tetrachloro Methane	CCl ₄	62	1,2,4-Trichloro Benzene	1,2,4-C ₆ H ₃ Cl ₃
31	Benzene	C ₆ H ₆	63	Hexachloro-1,3-Butadiene	1,3-C ₄ Cl ₆
32	1,2-Dichloro Ethane	1,2-C ₂ H ₄ Cl ₂			
33	n-Heptane	n-C ₇ H ₁₆ = C7			

Table 1 – list of molecules in standard gas bottle

LIST OF COMPOUNDS

The list of compounds is defined in the VISTACHROM Software. It allows an automatic calculation of the concentration for each molecule by taking into account a response factor determined with the internal calibration reference. This provides a strong advantage: gas cylinders of specific standards are no more required, it is no more necessary to perform calibration for each molecule. A screenshot of the software is given hereafter.

#	Name	RT Min	RT Max	Select Peak	GC Result formula	With X=
1	PROPENE	14	22	Middle	X	Area/BS
2	FREON-12	28	36	Middle	12,5 * X	Area/BS
3	FREON-114	36	38	Middle	30 * X	Area/BS
4	CHLOROMETHANE	38	46	Middle	3 * X	Area/BS
5	VINYLCHLORIDE	46	49	Middle	1,5 * X	Area/BS
6	1-3-BUTADIENE	49	54	Middle	0,96 * X	Area/BS
7	BROMOMETHANE	80	87	Middle	2 * X	Area/BS
8	CHLOROETHANE	91	97	Middle	4 * X	Area/BS
9	FREON-11	112	122	Middle	12,5 * X	Area/BS
10	ETHANOL	144	154	Middle	2,43 * X	Area/BS
11	ACROLEIN	162	166	Middle	1,7 * X	Area/BS
12	1-1-DICHLOROETHENE	166	176	Middle	3 * X	Area/BS
13	FREON-113	174	175	Middle	30 * X	Area/BS
14	ACETONE	184	194	Middle	2,29 * X	Area/BS
15	CS2	194	196	Middle	9 * X	Area/BS
16	IPA	204	212	Middle	2,11 * X	Area/BS
17	DICHLOROMETHANE	233	241	Middle	3 * X	Area/BS
18	T-1-2-DICL-ETHENE	258	264	Middle	4,5 * X	Area/BS
19	MTBE	263	267	Middle	3 * X	Area/BS
20	N-HEXANE	282	290	Middle	1,08 * X	Area/BS
21	1-1-DICHLOROETHANE	310	318	Middle	3,32 * X	Area/BS
22	VINYL ACETATE	318	325	Middle	3 * X	Area/BS
23	C-1-2-DICL-ETHENE	380	385	Middle	4,3 * X	Area/BS
24	ETHYLACETATE	385	388	Middle	2,95 * X	Area/BS
25	MEK	388	396	Middle	1,84 * X	Area/BS
26	THF	409	418	Middle	2 * X	Area/BS
27	CHLOROFORME	421	425	Middle	10 * X	Area/BS
28	111-TriCL-ETHANE	426	428	Middle	7,5 * X	Area/BS
29	CYCLOHEXANE	428	435	Middle	1,06 * X	Area/BS
30	CCl4	442	450	Middle	9 * X	Area/BS
31	BENZENE	473	483	Middle	X	Area/BS
32	1-2-DICHLOROETHANE	484	494	Middle	4,33 * X	Area/BS
33	N-HEPTANE	497	507	Middle	1,05 * X	Area/BS
34	TRICHLOROETHENE	553	561	Middle	4,31 * X	Area/BS
35	1-2-DICL-PROPANE	587	595	Middle	3,23 * X	Area/BS
36	ME-METHACRYLATE	604	610	Middle	2,9 * X	Area/BS
37	1-4-DIOXANE	611	619	Middle	2 * X	Area/BS
38	BROMO-DICL-METHAN	621	628	Middle	5 * X	Area/BS
39	T-1-3-DICL-PROPEN	677	685	Middle	4,19 * X	Area/BS
40	MIBK	700	708	Middle	2 * X	Area/BS
41	TOLUENE	710	719	Middle	1,05 * X	Area/BS
42	C-1-3-DICL-PROPEN	752	760	Middle	5,15 * X	Area/BS
43	112-TriCL-ETHANE	772	774	Middle	5,39 * X	Area/BS
44	TETRACHLOROETHENE	771	779	Middle	5,1 * X	Area/BS
45	MBK	802	809	Middle	2 * X	Area/BS
46	DIBR-CL-METHANE	814	821	Middle	5 * X	Area/BS
47	1-2-DIBROMOETHANE	827	835	Middle	9 * X	Area/BS
48	CHLOROBENZENE	881	891	Middle	1,47 * X	Area/BS
49	ETHYLBENZENE	891	901	Middle	1,1 * X	Area/BS
50	m,p-XYLENES	905	914	Middle	1,1 * X	Area/BS
51	O-XYLENE	950	958	Middle	1,1 * X	Area/BS
52	STYRENE	957	965	Middle	1,1 * X	Area/BS
53	BROMOFORM	979	987	Middle	9 * X	Area/BS
54	1122TetraCL-ETHAN	1038	1046	Middle	6 * X	Area/BS
55	P-ETHYLTOLUENE	1054	1062	Middle	1,04 * X	Area/BS
56	135-TMB	1061	1069	Middle	1,15 * X	Area/BS
57	124-TMB	1102	1110	Middle	1,15 * X	Area/BS
58	1-3-DICL-BENZENE	1136	1144	Middle	2,3 * X	Area/BS
59	1-4-DICL-BENZENE	1147	1155	Middle	2,3 * X	Area/BS
60	BENZYLCHLORIDE	1163	1172	Middle	1,2 * X	Area/BS
61	1-2-DICL-BENZENE	1189	1197	Middle	2,3 * X	Area/BS
62	124-TriCL-BENZENE	1374	1382	Middle	3,4 * X	Area/BS
63	HexCL-1-3BUTADIEN	1386	1396	Middle	6,3 * X	Area/BS

Figure 1 – list of molecules / substances table from VISTACHROM

CHROMATOGRAMS

The chromatograms illustrates the capabilities of the equipment to monitor the list of compounds. Analysis is done **in 40 minutes**

With special application, the methanol may be identified and quantified at retention time (RT) of 75 seconds

We can note that Vinyl acetate is located after 1-1 di-chloroethane with a RT of 320 seconds.

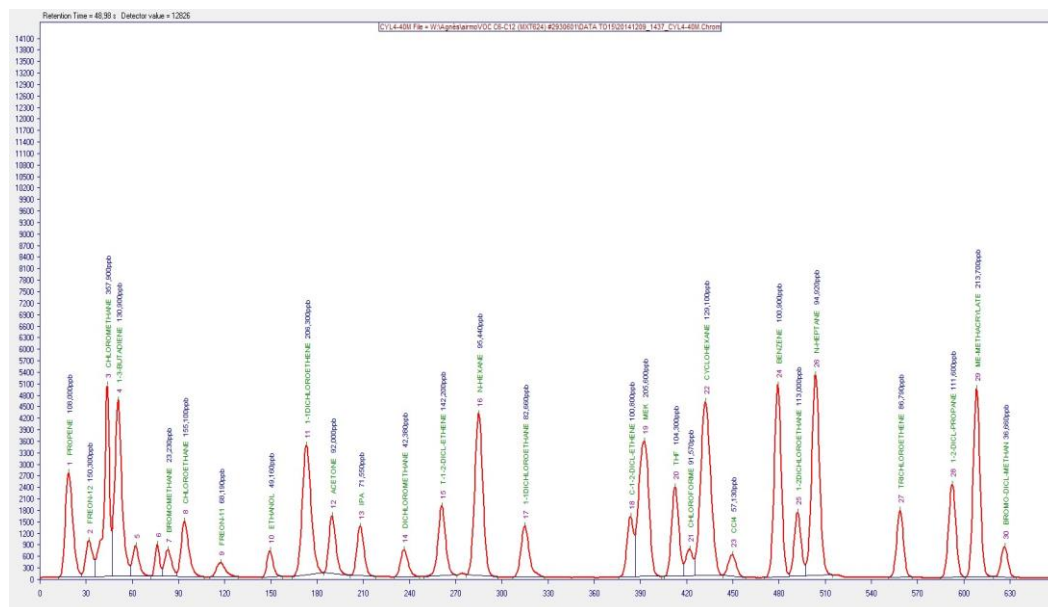


Figure 2 - Chromatogram – area 1

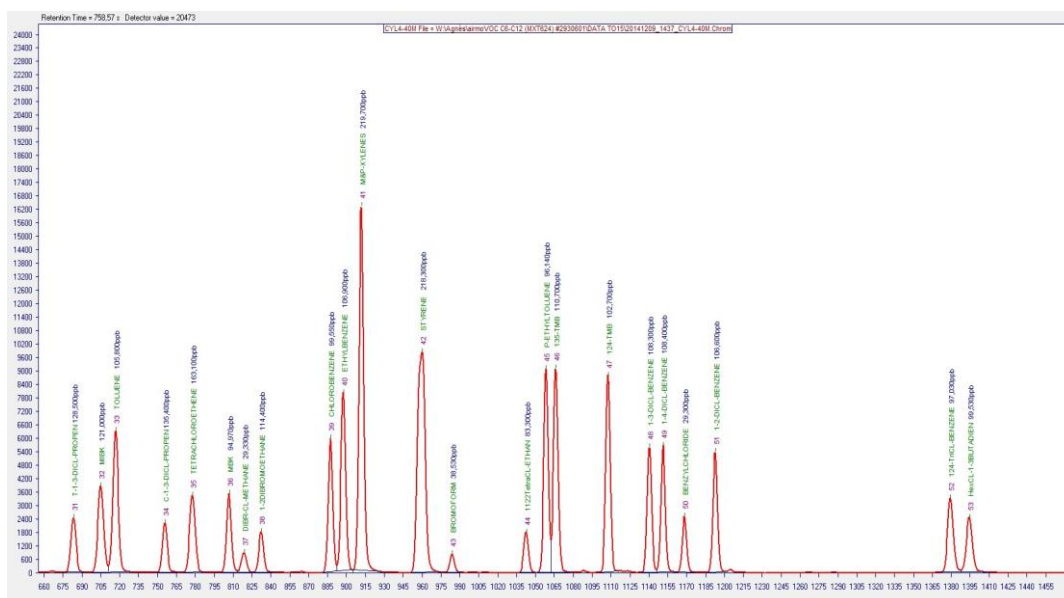


Figure 3 – chromatogram area 2

RESULTS

The following table shows that the Chromatotec® solution is able to identify and quantify the list of molecules. It gives details about the type of instruments offering the best separation.

On the list, we can discover:

- 13 new Oxygenated Volatile Organic Compounds (OVOC)
- 4 new Halogenated VOC (XVOC)

More than 7 compounds are analyzed on airmo VOC C₂C₆ and 7 couples of molecules may offer coelution effect with same RT. In spite of this coelution, the quantification is very good for m- and p-xylene analyzed with airmoVOC C₆C₁₂.

The CS₂ can be analyzed by Chroma S analyzer using FPD detector.

No.	Component	Chemical Formula	Identified by configuration	Coelution between the compounds	Remarks
1	PROPENE	C ₃ H ₆	airmoVOC C ₂ C ₆	Coelution between the compounds	
2	Dichloro Difluoro Methane	CCL ₂ F ₂ = F12	airmoVOCC ₂ C ₆		TO 14 included
3	12 Dichlorotetrafluoro Ethane	C ₂ CL ₂ F ₄ = F114	airmoVOCC ₂ C ₆		TO 14 included
4	Chloro Methane	CH ₃ -Cl	airmoVOCC ₂ C ₆		TO 14 included
5	Vinyl Chloride	C ₂ H ₃ Cl	airmoVOCC ₂ C ₆		TO 14 included
6	13-Butadiene	1,3-C ₄ H ₆	airmoVOCC ₂ C ₆		TO 14 included
7	Bromo Methane	CH ₃ -Br	airmoVOC ₆ 24		TO 14 included
8	Chloro Ethane	C ₂ H ₅ -CL	airmoVOC ₆ 24		TO 14 included
9	Trichloro Fluoro Methane	CCL ₃ -F = F11	airmoVOC ₆ 24		TO 14 included
10	Ethanol	C ₂ H ₅ -OH	airmoVOC ₆ 24		NEW OVOC
11	Acrolein	CH ₂ :CHCHO	Obtained by calculation	CO_1	NEW OVOC
12	11-Dichloro Ethene	1,1-C ₂ H ₂ Cl ₂	airmoVOCC ₆ C ₁₂	CO_1	TO 14 included
13	112Trichlorotrifluoro Ethane	C ₂ CL ₃ F ₃ = F113	airmoVOCC ₂ C ₆		NEW OVOC
14	Acetone	(CH ₃) ₂ CO	airmoVOC ₆ 24		NEW OVOC
15	Carbon Disulfide	CS ₂	chromaS		Analyzed by Chroma S
16	2-Propanol = IPA	i-C ₃ H ₇ -OH	airmoVOC ₆ 24		NEW OVOC
17	Dichloro Methane	CH ₂ Cl ₂	airmoVOC ₆ 24		TO 14 included
18	t-12-Dichloro Ethene	t-1,2-C ₂ H ₂ Cl ₂	airmoVOC ₆ 24	CO_2	NEW XVOC
19	Methyl-Tert-Butyl Ether = MTBE	tert-C ₄ H ₉ OCH ₃	airmoVOC ₆ 24	CO_2	NEW OVOC
20	N-Hexane	n-C ₆ H ₁₄ = C ₆	airmoVOCC ₆ C ₁₂		
21	11-Dichloro Ethane	1,1-C ₂ H ₄ Cl ₂	airmoVOCC ₆ C ₁₂		TO 14 included
22	Vinyl Acetate	CH ₃ COOC ₂ H ₃	airmoVOC ₆ 24		NEW OVOC
23	c-12-Dichloro Ethene	cis-1,2-C ₂ H ₂ Cl ₂	airmoVOCC ₆ C ₁₂		TO 14 included
24	Ethyl Acetate	CH ₃ COOC ₂ H ₅	Obtained by calculation	CO_3	NEW OVOC
25	2-Butanone = MEK	CH ₃ COC ₂ H ₅	airmoVOCC ₆ C ₁₂	CO_3	NEW OVOC
26	Tetrahydrofuran = THF	(CH ₂) ₄ O	airmoVOC ₆ 24		NEW OVOC
27	Chloroform	CHCl ₃	airmoVOC ₆ 24		TO 14 included
28	111-Trichloro Ethane	1,1,1-C ₂ H ₃ Cl ₃	airmoVOCC ₆ C ₁₂	CO_4	TO 14 included
29	Cyclohexane	(CH ₂) ₆	airmoVOCC ₆ C ₁₂	CO_4	
30	Tetrachloro Methane	CCl ₄	airmoVOC ₆ 24		TO 14 included
31	Benzene	C ₆ H ₆	airmoVOCC ₆ C ₁₂		TO 14 included
32	12-Dichloro Ethane	1,2-C ₂ H ₄ Cl ₂	airmoVOCC ₆ C ₁₂		TO 14 included
33	N-Heptane	n-C ₇ H ₁₆ = C ₇	airmoVOCC ₆ C ₁₂		
34	Trichloro Ethylene	C ₂ HCl ₃	airmoVOCC ₆ C ₁₂		TO 14 included
35	12-Dichloro Propane	1,2-C ₃ H ₆ Cl ₂	airmoVOC ₆ 24		TO 14 included
36	Methyl Methacrylate	CH ₂ :C(CH ₃)COOCH ₃	airmoVOCC ₆ C ₁₂	CO_5	NEW OVOC
37	14-Dioxane	C ₄ H ₈ O ₂	calcul	CO_5	NEW OVOC
38	Bromo Di Chloro Methane	CHBrCl ₂	airmoVOC ₆ 24		XVOC

No.	Component	Chemical Formula	Identified by configuration	Coelution between the compounds	Remarks
39	t-13-Dichloro Propene	trans-1,3-C ₃ H ₄ Cl ₂	airmoVOCC6C12		TO 14 included
40	4-Methyl-2-Pentanone = MIBK	C ₄ H ₉ COCH ₃	airmoVOC624		NEW OVOC
41	Toluene	C ₇ H ₈	airmoVOCC6C12		TO 14 included
42	c-13-Dichloro Propene	cis-1,3-C ₃ H ₄ Cl ₂	airmoVOCC6C12		TO 14 included
43	112-Trichloro Ethane	1,1,2-C ₂ H ₃ Cl ₃	airmoVOCC6C12	CO_6	TO 14 included
44	Tetrachloro Ethene	C ₂ Cl ₄ = PER	airmoVOCC6C12	CO_6	TO 14 included
45	2-Hexanone = MBK	CH ₃ (CH ₂) ₃ COCH ₃	airmoVOC624		NEW OVOC
46	Di Bromo Chloro Methane	CHBr ₂ Cl	airmoVOC624		XVOC
47	12-Dibromo Ethane	1,2-CH ₂ CH ₂ Br ₂	airmoVOCC6C12		TO 14 included
48	Chlorobenzene	C ₆ H ₅ Cl	airmoVOCC6C12		TO 14 included
49	Ethylbenzene	C ₆ H ₅ CH ₂ H ₅	airmoVOCC6C12		TO 14 included
50	p-Xylene	p-C ₆ H ₄ (CH ₃) ₂	airmoVOCC6C12	CO_7	TO 14 included
50	m-Xylene	m-C ₆ H ₄ (CH ₃) ₂	airmoVOCC6C12	CO_7	TO 14 included
51	o-Xylene	o-C ₆ H ₄ (CH ₃) ₂	airmoVOCC6C12	CO_8	TO 14 included
52	Styrene	C ₆ H ₅ CHCH ₂	airmoVOCC6C12	CO_8	TO 14 included
53	Bromoform	CHBr ₃	airmoVOC624		XVOC
54	1122-Tetrachloro Ethane	1,1,2,2-C ₂ H ₂ Cl ₄	airmoVOC624		TO 14 included
55	4-Ethyl Toluene	p-(C ₂ H ₅)C ₆ H ₄ CH ₃	airmoVOCC6C12		TO 14 included
56	135-Trimethyl Benzene	1,3,5-C ₆ H ₃ (CH ₃) ₃	airmoVOCC6C12		TO 14 included
57	124-Trimethyl Benzene	1,2,4-C ₆ H ₃ (CH ₃) ₃	airmoVOCC6C12		TO 14 included
58	13-Dichloro Benzene	1,3-C ₆ H ₄ Cl ₂	airmoVOCC6C12		TO 14 included
59	14-Dichloro Benzene	1,4-C ₆ H ₄ Cl ₂	airmoVOC624		TO 14 included
60	Benzyl Chloride	C ₆ H ₅ CH ₂ Cl	airmoVOC624		TO 14 included
61	12-Dichloro Benzene	1,2-C ₆ H ₄ Cl ₂	airmoVOCC6C12		TO 14 included
62	124-Trichloro Benzene	1,2,4-C ₆ H ₃ Cl ₃	airmoVOCC6C12		TO 14 included
63	Hexachloro-13-Butadiene	1,3-C ₄ Cl ₆	airmoVOCC6C12		TO 14 included

Table 2 – configuration type for molecules identification

CONCLUSIONS

With the combination of airmoVOC 624 and airmoVOC C₆C₁₂ analyzers, it is possible to target 55 compounds of the 63 molecules of the list. If we focus on CS₂, this molecule can be analyzed by ChromaS. In addition this analyzer allows to measure H₂S, SO₂, Mercaptans, etc).

With airmoVOC 624: 55 compounds are analyzed too but considering the coelution, 48 offer peaks with high resolution and the capability of the system to quantify in addition the Vinyl acetate.

Considering nitrogenous compounds (Amines), the Acrylonitrile (CH₃CH₂CN), listed on TO14 can also be analyzed on airmoVOC C₆C₁₂. Aniline /Phenyl amine / Amino Benzene is a Toxic organic aromatic compound C₆H₅-NH₂, as Nitro Benzene, it can be analyzed on airmoVOC C₆C₁₂ with RT located after di-ethyl Benzene. With the association of the 3 technologies the capacities of these configuration are huge for ambience or industry markets.

Contact us: 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