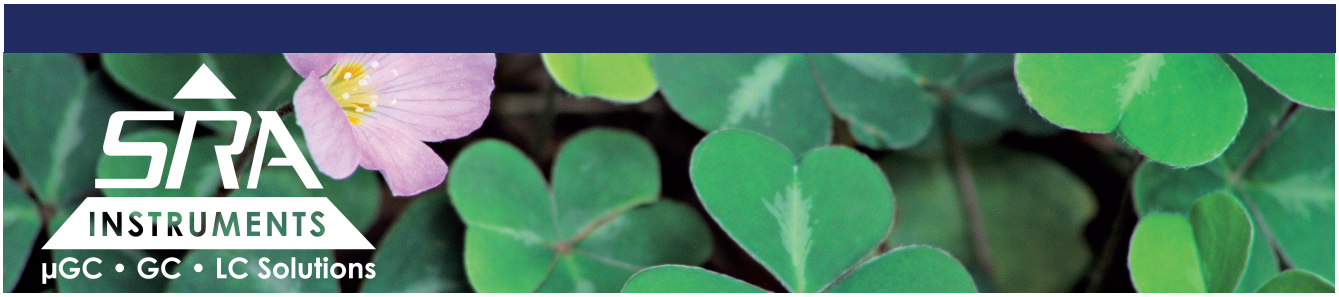


Determination of VOC's in aqueous samples by using Purge & Trap – GCMSD

INTRODUCTION

The regulatory governing the controls and the legal limits for the analysis of volatile organic compounds (VOC's) in water and soil are becoming more and more stringent. In particular the Italian DLGS 152/2006 and upgrades set the detection limits for some compounds, in the order of 1 ppt.

Typically, these analyses met EPA (Environmental Protection Agency) methods guidelines.
In particular, EPA method 8260 requires the use of the GC-MS as separation-detection technique, and EPA method 5030 for the Purge & Trap extraction technique.

The addition of a cryofocusing step, after the concentration of the sample through the P&T technique, is often used in order to achieve the above limits.
Cryofocusing involves the use of liquid nitrogen, which is expensive and not easily handled.

The goal of this work is to achieve the limit of 1 ppt, for the compounds 1,2-Dibromoethane and 1,2,3-trichloropropane in aqueous matrices avoiding the Cryofocusing step.

INSTRUMENTATION

- P&T EST Analytical ENCON Evolution
- Water Autosampler EST Analytical CENTURION
- GC Agilent Technologies 7890B
- MSD Agilent Technologies 5977A, Ion Source Extractor

- The configuration also allows the direct liquid injection by using Agilent 7693 autosampler.

ANALYTICAL DETERMINATION

Analysis of VOC in water samples down to sub ppt level, using P&T, S/SL injector and MSD detector

- ENCON Evolution: Sparger 25 ml
- CENTURION: Sampling and internal standards addition
- GC 7890: injector S/SL, split ratio 1:10
- Column DB-624 Ultra Inert 20mX180µmX1.0µm flow 0.8 ml / min
- MSD 5977A Extract Ion ETUNE.U
- Acquisition: S.I.M.

OPERATIONAL PROCEDURE

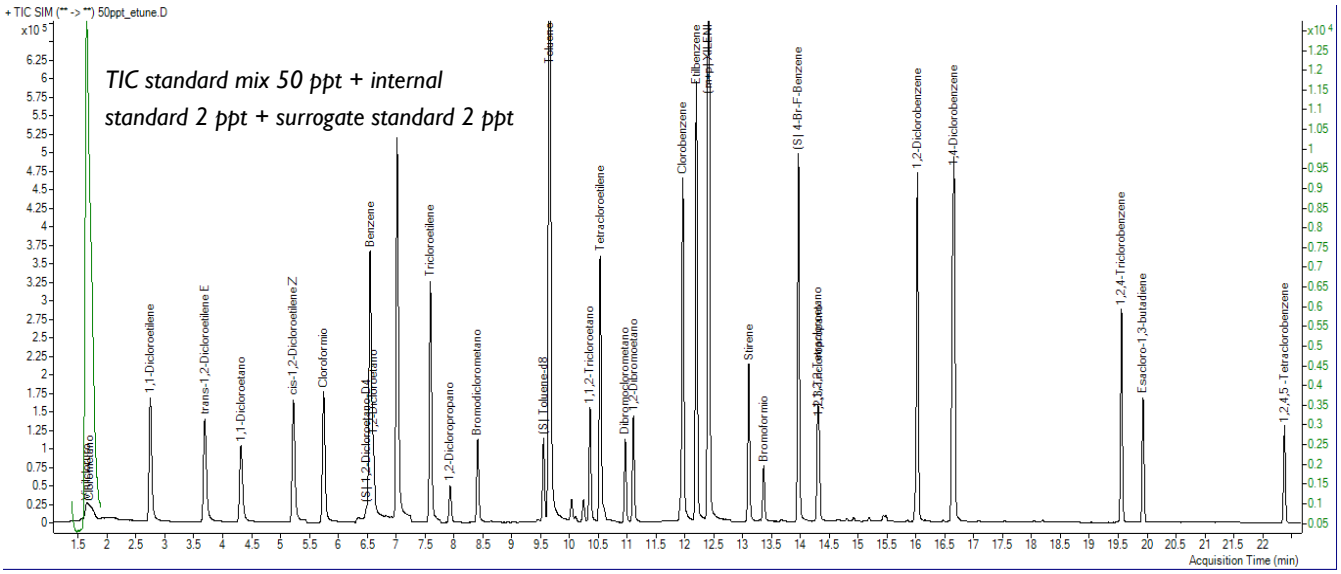
Six calibration levels (0.1-1-5-10-20-50 ppt) in water were prepared from a standard mix VOC, in methanol at 200 mg/L.
The response for each analyte was normalized by using a mix of internal standards containing respectively: Fluorobenzene, Chlorobenzene-d5 and 1,4-Dichlorobenzene-d4.

Each sample has been added automatically by autosampler CENTURION with 5 µl of a 10 ppb internal standard mix in methanol.

The final concentration of the internal standard in the sample is thus equal to 2ppt.
To each sample has been added a standard surrogate mix, containing respectively:
- 1,2-Dichloroethane-d4,
- Toluene-d8 and
- 4-Bromofluorobenzene,

in the same conditions and concentrations of the standards mix.

All the analytes provide a linear calibration curves (origin: ignore, no weighting).

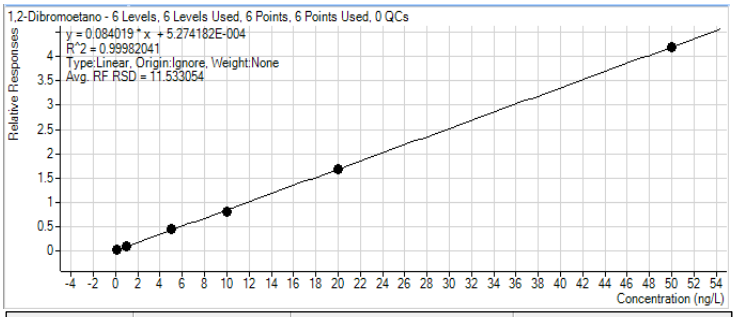


Analyte standard mix + internal standard (i.s.) + surrogate standard (S)

COMPOUND	ACQ MODE	TYPE	RT (min)	CF R^2
Vinyl chloride	SIM	Target	1.64	0.999
1,1-Dichloroethylene	SIM	Target	2.75	0.997
trans-1,2-Dichloroethylene E	SIM	Target	3.69	0.997
1,1-Dichloroethane	SIM	Target	4.31	0.999
cis-1,2-Dichloroethylene Z	SIM	Target	5.22	1.000
Chloroform	SIM	Target	5.75	1.000
(S) 1,2-Dichloroethane-d4	SIM	Surrogate	6.49	xxx
Benzene	SIM	Target	6.55	1.000
1,2-Dichloroethane	SIM	Target	6.60	1.000
(I.S.) Fluorobenzene	SIM	ISTD	7.02	xxx
Trichloroethylene	SIM	Target	7.59	1.000
1,2-Dichloropropane	SIM	Target	7.93	0.999
Bromodichloromethane	SIM	Target	8.41	0.999
(S) Toluene-d8	SIM	Surrogate	9.55	xxx
Toluene	SIM	Target	9.66	0.998
1,1,2-Trichloroethane	SIM	Target	10.36	0.999
Tetrachloroethylene	SIM	Target	10.53	1.000
Dibromochloromethane	SIM	Target	10.97	1.000
1,2-Dibromoethane	SIM	Target	11.11	0.999
(I.S.) Chlorobenzene - d5	SIM	ISTD	11.92	xxx
Chlorobenzene	SIM	Target	11.97	1.000
Ethylbenzene	SIM	Target	12.20	0.998
(m + p) XYLENES	SIM	Target	12.41	0.997
Styrene	SIM	Target	13.11	1.000
Bromoform	SIM	Target	13.36	0.999
(S) 4-Br-F-Benzene	SIM	Surrogate	13.97	xxx
1,1,2,2-Tetrachloroethane	SIM	Target	14.30	0.999
1,2,3-Trichloropropane	SIM	Target	14.32	0.999
1,2-Dichlorobenzene	SIM	Target	16.02	1.000
(I.S.) 1,4-Dichlorobenzene-d4	SIM	ISTD	16.63	xxx
1,4-Dichlorobenzene	SIM	Target	16.66	1.000
1,2,4-Trichlorobenzene	SIM	Target	19.56	1.000
Hexachloro-1,3-butadiene	SIM	Target	19.93	0.999
1,2,4,5 -Tetrachlorobenzene	SIM	Target	22.38	1.000

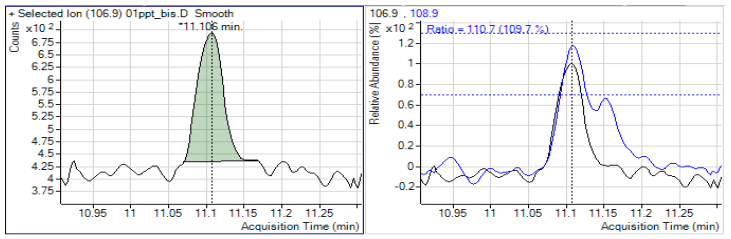
CALIBRATION CURVES

1,2-Dibromoethane, calibration curve: R^2=0.999

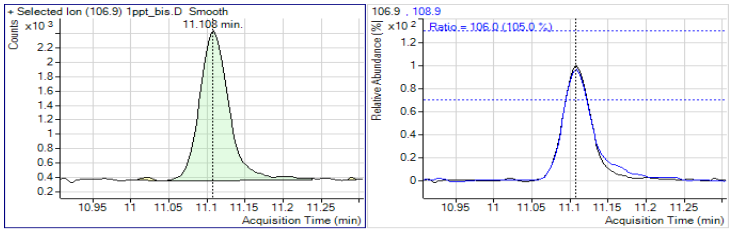


Sample			1,2-Dibromoetano Method	1,2-Dibromoetano Results				(i.s.) Clorobenzene - d5 (ISTD) Results	
Name	Type	Level	Exp. Conc.	RT	Resp.	Final Conc.	Accuracy	RT	Resp.
01ppt	Cal	1	0.1000	11.106	607	0.1227	122.7	11.917	56008
1ppt	Cal	2	1.0000	11.108	5574	1.1327	113.3	11.919	58241
5ppt	Cal	3	5.0000	11.106	24503	5.2618	105.2	11.917	55360
10ppt	Cal	4	10.0000	11.107	45036	9.5205	95.2	11.917	56265
20ppt	Cal	5	20.0000	11.106	94129	19.9922	100.0	11.919	56021
50ppt	Cal	6	50.0000	11.106	231717	50.0702	100.1	11.919	55074

1,2-Dibromoethane, 0.1 ppt standard peak



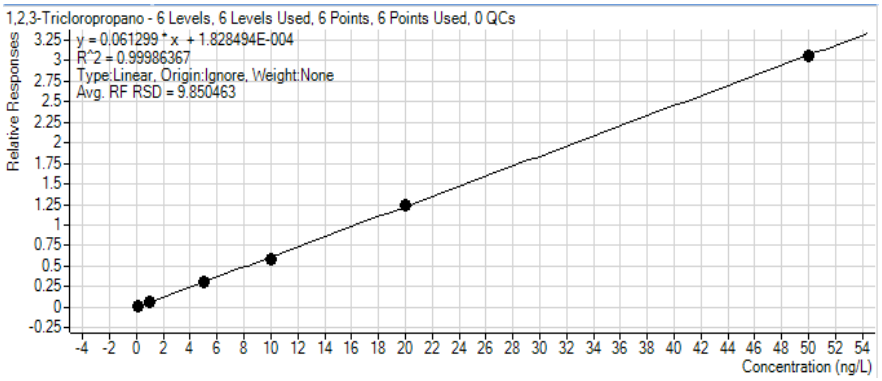
1,2-Dibromoethane, 1 ppt standard peak



CALIBRATION CURVES

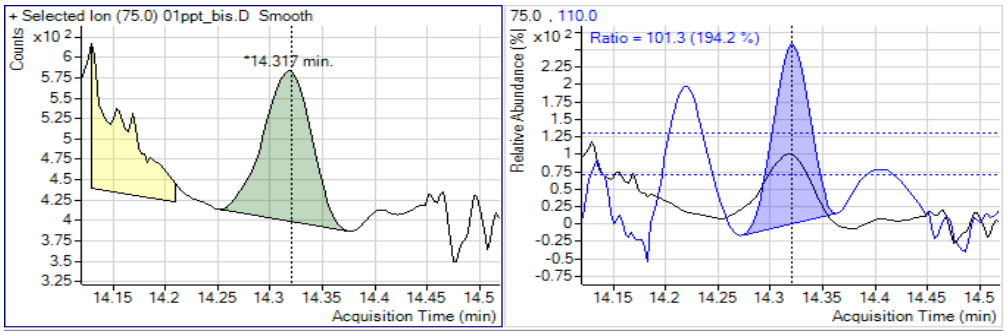
1,2,3-Trichloropropane, calibration curve:

R^2=0.999

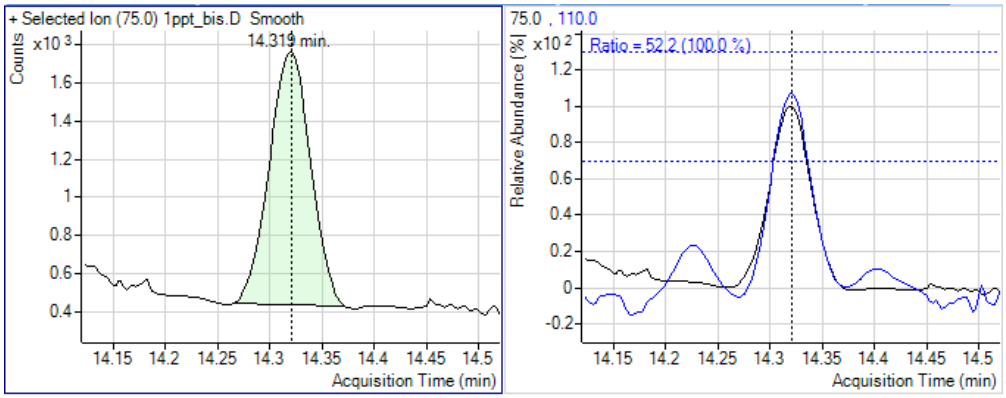


Sample			1,2,3-Tricloropropano Method	1,2,3-Tricloropropano Results				(i.s.) Clorobenzene - d5 (ISTD) Results	
Name	Type	Level	Exp. Conc.	RT	Resp.	Final Conc.	Accuracy	RT	Resp.
01ppt	Cal	1	0.1000	14.317	429	0.1220	122.0	11.917	56008
1ppt	Cal	2	1.0000	14.319	3653	1.0203	102.0	11.919	58241
5ppt	Cal	3	5.0000	14.319	17486	5.1497	103.0	11.917	55360
10ppt	Cal	4	10.0000	14.320	33114	9.5981	96.0	11.917	56265
20ppt	Cal	5	20.0000	14.319	69520	20.2415	101.2	11.919	56021
50ppt	Cal	6	50.0000	14.319	167187	49.5196	99.0	11.919	55074

1,2,3-Trichloropropane, 0.1 ppt standard peak



1,2,3-Trichloropropane, 1 ppt standard peak



ACCURACY

All calibration points showed an accuracy range between 80 and 120%, except for the point at 0.1 ppt, which showed an accuracy of 123% for 1,2-Dibromoethane and 122% for 1,2,3-Trichloropropane

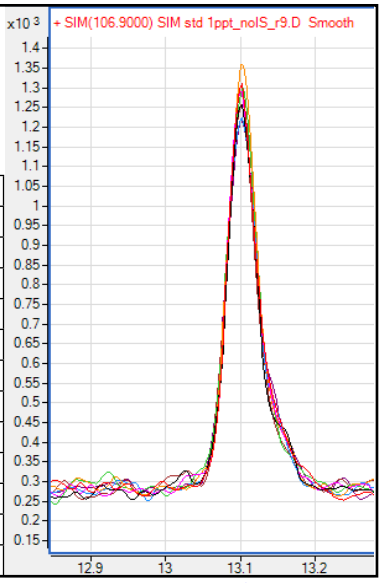
REPEATABILITY

The injection in series (8 repetitions) of the 1 ppt standard mix provided repeatability values, calculated as RSD% (absolute areas response) equal to 2.0% for 1,2-Dibromoethane and 1.8% for 1,2,3 -Trichloropropane.

1,2-Dibromoethane,

1 ppt standard peak

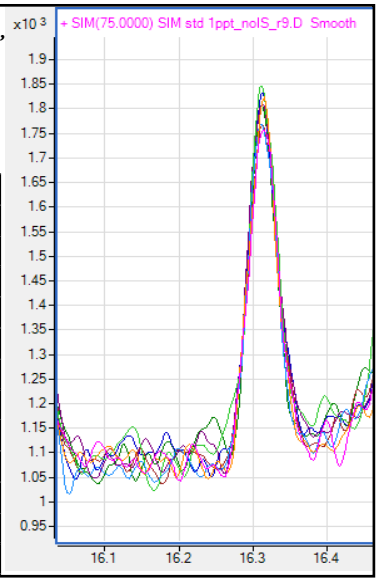
Name	Resp.
std 1ppt_r1	3195
std 1ppt_r2	3163
std 1ppt_r3	3123
std 1ppt_r4	3227
std 1ppt_r5	3193
std 1ppt_r6	3252
std 1ppt_r7	3059
std 1ppt_r8	3135
MEAN	3168.4
STD.DEV	62.0
RSD%	2.0



1,2,3-Trichloropropane,

1 ppt standard peak

Name	Resp.
std 1ppt_r1	1933
std 1ppt_r2	1940
std 1ppt_r3	1922
std 1ppt_r4	1898
std 1ppt_r5	1851
std 1ppt_r6	1949
std 1ppt_r7	1893
std 1ppt_r8	1875
MEAN	1907.6
STD.DEV	34.2
RSD%	1.8



INTERNAL STANDARD REPEATABILITY

The internal standard repeatability, (I.S. automatically added by the system CENTURION), was calculated as % RSD of the responses of the absolute areas (relative to the calibration curve) and gave the results reported in the table.

	(I.S.) Fluorobenzene	*(I.S.) Chlorobenzene - d5*	*(I.S.) 1,4-Dichlorobenze-d4*
Conc.	**Resp.**	**Resp.**	**Resp.**
0.1ppt	1882699	56008	672325
1ppt	1955681	58241	690686
5ppt	1852340	55360	670669
10ppt	1871410	56265	682260
20ppt	1884255	56021	683386
50ppt	1850496	55074	655401
MEAN	1882813.5	56161.5	675787.8
STD.DEV	38509.4	1113.9	12453.1
RSD%	2.0	2.0	1.8

CONCLUSIONS

The instrumental solution used in this experiment was:

Purge & Trap EST Analytical CENTURION / ENCON and GC / MSD, Agilent Technologies 7890B / 5977A, their performances allowed to reach the limit of 1 ppt for 1,2-Dibromoethane and 1,2,3-Trichloropropane in aqueous matrices, as required by current environmental regulations, with a high level of confidence as 0.1 ppt could be easily detected.

The new Extract Ion Source (Agilent Technologies 5977A) and the innovative sample path (EST Analytical ENCON), significantly contributed to the achievement of such results

The extraction efficiency of the system CENTURION / ENCON was evaluated by comparison with a VOC standard mix analyzed by direct injection, in the same calibration range.

0.1-1-5-10-20 ppt analyzed by the system CENTURION / ENCON from a 25 ml volume, correspond to a concentration of 2.5-25-125-250-500 ppb for a volume of 1ul directly injected by Agilent Technologies 7693 autosampler.

The obtained data showed responses in the same order of magnitude confirming the Purge&Trap extraction efficiency.

SRA Purge & Trap – GCMSD solution tested at dtoLABS (Agilent Technologies Analytical Excellence Center, Authorized Partnerlab)

dtoLABS Analytical Excellence Center

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