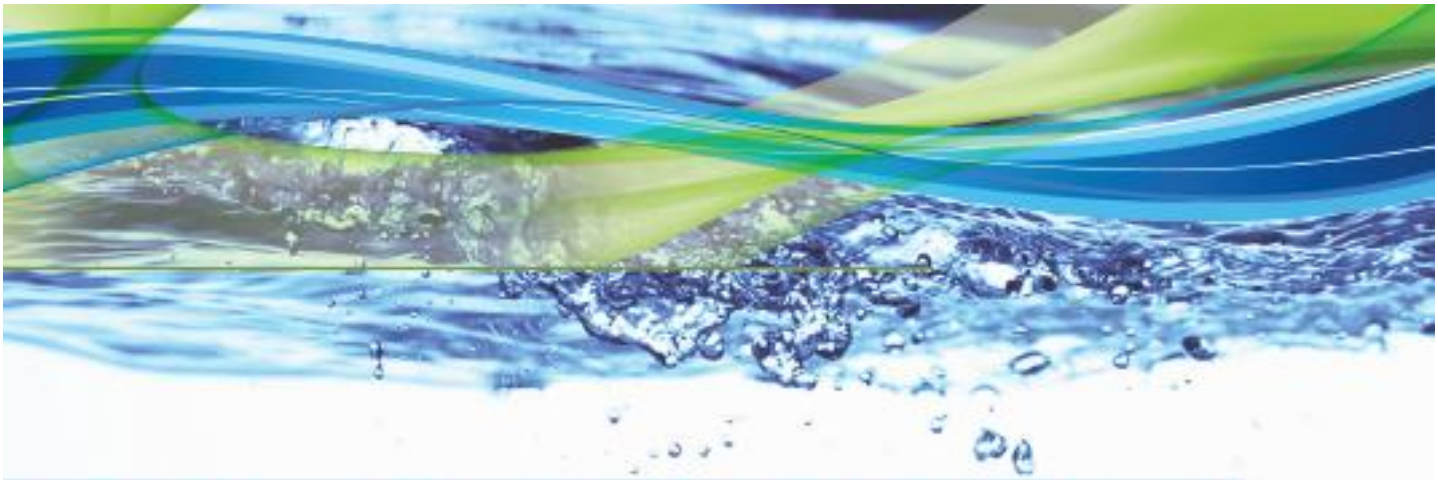

Purge&Trap Extraction of Volatiles in Drinking Water and High Speed TOF MS Detection in compliance to EPA 524.3

APPLICATION NOTE

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Introduction

Analysis of Volatiles Organic Compounds (VOCs) in water is of increasing interest due to critical ground contamination from several sources as gasoline, oil spills and industrial solvents.
Especially for drinking water, possible contamination is of great concern for potential human health effect. The U.S. Environmental Protection Agency (EPA) strictly regulates the assessment of drinking water quality through method 524.3 in which detection limits and instrumentation requirements are established. Official guidelines require the monitoring of VOCs contaminants in drinking water at progressively lower concentration level and typically the P&T extraction technique is indicated to reach the requested limit of detection.
This work is presenting the use of the flexible DANI Master Purge&Trap Sampler (Master P&T), highlighting the several benefits of this SYSTEMin terms of extended automation, overlapping incubation time capability and absence of cross-contamination between samples.
Besides, particular attention has been paid to the most volatiles compounds in terms of peak shape and recovery.

Figure 1 : Master P&T coupled to the Master GC-TOF MS

Method

In this work the Purge&Trap extraction method, coupled with a GC-TOF MS analysis, is described to determine VOCs in water.

The system is illustrated in **Figure 1**. Coupling the Purge&Trap with an automatic sampler guarantees a good repeatability in terms of internal standard addition, assuring a complete automation of all operation steps.

In **Figure 2** the schematic plumbing of the P&T is illustrated. The use of a triple layer sorbent trap has been found to be ideal to handle the wide range of volatility and polarity represented by the compounds under study.

The use of the Master TOF MS as detector offers the possibility to discriminate even between coelute compounds exploiting the Deconvolution Algorithm of MasterLab Processing software.

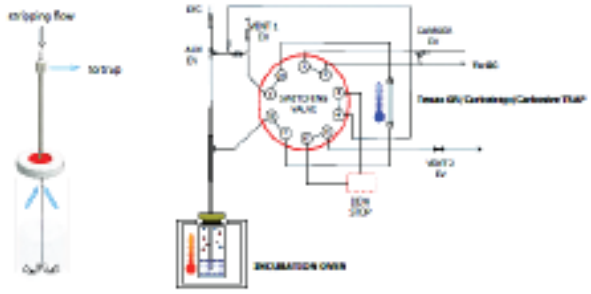


Figure 2: Dynamic Headspace and Purge&Trap Sampler schematic plumbing in the "trapping" phase

Sample Preparation

Calibration standard mixtures and fortified blanks have been prepared following the method guideline,

starting from commercial certified VOCs mixture in methanol as stock solution.

A Primary Dilution Standard in methanol has been used to spike 10 mL of organic-free water (HPLC grade) directly into the vial to prepare calibration standards for linearity evaluation in the range of 0.02 to 50 µg/L. Internal Standard required from EPA method 524.3 were added in a final concentration of 2 ppb to each sample, using MasterAS.

According to quality control criteria, before calibration, the TOF-MS has been checked to meet tuning requirement by injecting 4-bromofluorobenzene (BFB). All the ion ratio criteria is achieved after a standard tuning of the system. (**Figure 8**)

Master GC	
Column	vocol 20 m, 0.18 mm, 1µm
Flow Rate	0.8 mL/min
SSL Temp	250°C
Oven Temp	35 (5 min) to 240°C (2 min) at 20°C/min

Master TOF	
Transfer Line Temp	250°C
EI source	70 eV
Source Temperature	200°C
Mass Range	35-260 amu
Aquisition Rate	5 spectra/s

Master DHS/P&T in Purging Mode	
Sample Volume	5 mL
Incubation Temp	60°C
Stripping	5 min @ 100 mL/min of Helium
Trap Temp	-10°C
Dew Stop Temp	0°C
Trap Desorption Temp	280°C
Injection Time	2 min
Transfer Line Temp	250°C
Valve Temp	250°C
Baking Time	10 min @ 80 mL/min
Trap Baking Temp	285°C
Dew Stop Baking Temp	190°C
Trap Sorbent	Tenax/ Carbotrap/ Carbosieve

Table 1: Operative Conditions

Results and Discussion

Faster separation has been obtained by using a shorter and narrow bore column compared to conventional approach using longer column. In **Figure 4** the TIC of a mixture containing 52 compounds (listed in **Table 2**) is reported. Using a 20m column with an id of 0.18mm it is possible to complete the separation in about **14 minutes**, however several compounds appear partially or completely coeluted. The advantage of using the TOF MS detector is the possibility to discriminate within coeluted compounds due to powerful deconvolution capability. With DANI MasterLAB processing software (MLP) it is possible to locate

different apexes under the same TIC peak, allowing the proper identification of coeluted compounds. As an example, Figure 4 shows the deconvolution results for the peak at RT 9.93 min, with the identification of two different compounds.

RT	Compound Name	Integration Source	Linearity r^2	MDL (ppt)	EPA Limits (ppt)
4.520	Silane, 1,1-dichloro-	m/z61 (Semi Automatic)	0.998	9.84	40
6.330	Silane, 1,1-dichloro-	m/z63 (Semi Automatic)	0.993	1.91	20
7.017	cis-1,3-dichloropropene	m/z:61 (Semi Automatic)	0.998	2.48	42
7.280	Methane, bromochloro-	m/z: 128 (Semi Automatic)	0.998	2.61	42
7.337	Trichloromethane	m/z83 (Semi Automatic)	0.998	0.58	25
7.520	Silane, 1,1,1-trichloro-	m/z97 (Semi Automatic)	0.998	1.21	36
7.687	1-Propene, 1, 1-dichloro-	m/z: 75 (Semi Automatic)	0.998	2.15	82
7.725	Carbon Tetrachloride	m/z: 117 (Semi Automatic)	0.998	2.88	46
7.900	Benzene*	Ion: (deconvolution)	0.998	6.41	17
7.912	Silane, 1,2-dichloro*	Ion: (deconvolution)	0.993	7.54	25
8.210	IS1 Benzene, 1,4-difluoro-	m/z: 114 (Semi Automatic)	IS	IS	IS
8.455	Trichloroethylene	m/z130 (Semi Automatic)	0.998	1.31	25
8.633	Propane, 1,2-dichloro-	m/z63 (Semi Automatic)	0.998	1.88	10
8.752	Methane, dibromo-	m/z174 (Semi Automatic)	0.998	2.45	45
8.868	Methane, bromodichloro-	m/z83 (Semi Automatic)	0.998	0.85	14
9.220	cis-1,3-dichloropropene	m/z75 (Semi Automatic)	0.998	2.16	36
9.488	Toluene	m/z91 (Semi Automatic)	0.998	0.25	24
9.642	trans-1,3-dichloropropene	m/z75 (Semi Automatic)	0.998	9.84	32
9.795	Silane, 1,1,2-trichloro-	m/z97 (Semi Automatic)	0.997	0.98	40
9.915	Propane, 1,3-dichloro-*	Ion: (deconvolution)	0.998	5.83	30
9.928	Tetrachloroethylene*	Ion: (deconvolution)	0.998	1.28	36
10.198	Methane, dibromochloro-	m/z129 (Semi Automatic)	0.998	5.87	27
10.298	Silane, 1,2-dibromo-	m/z107 (Semi Automatic)	0.998	2.96	10
10.542	IS2 Chlorobenzene-d5	m/z117 (Semi Automatic)	IS	IS	IS
10.562	Benzene, chloro-	m/z112 (Semi Automatic)	0.998	0.58	19
10.628	Ethyl Benzene	m/z91 (Semi Automatic)	0.998	0.56	10
10.713	m/p-Xylene	m/z91 (Semi Automatic)	0.993	1.29	20
11.012	o-Xylene *	Ion: (deconvolution)	0.996	0.88	10
11.027	Styrene *	Ion: (deconvolution)	0.998	4.48	11
11.278	Isopropyl benzene	m/z105 (Semi Automatic)	0.997	0.67	11
11.580	Silane, 1, 1, 2, 2-tetrachloro-	m/z:83 (Semi Automatic)	0.998	5.41	13
11.538	Benzene, bromo-*	Ion: (deconvolution)	0.998	28.15	30
11.547	Propane, 1, 2, 3-trichloro-*	Ion: (deconvolution)	0.998	37.28	50
11.580	n-propyl Benzene	m/z91 (Semi Automatic)	0.998	9.76	77
11.688	2-chlorotoluene	m/z91 (Semi Automatic)	0.998	4.46	23
11.787	Benzene, 1,3,5-trimethyl-	m/z105 (Semi Automatic)	0.997	0.98	15
11.792	4-chlorotoluene	m/z91 (Semi Automatic)	0.997	0.85	14
11.955	Benzene, tert-butyl-	m/z119 (Semi Automatic)	0.998	0.54	20
11.990	Benzene, 1,3,5-trimethyl-	m/z105 (Semi Automatic)	0.998	0.51	NB
12.217	sec-butyl Benzene	m/z105 (Semi Automatic)	0.998	1.31	12
12.237	4-isopropyltoluene	m/z119 (Semi Automatic)	0.998	0.71	12
12.327	Benzene, 1,4-dichloro-	m/z146 (Semi Automatic)	0.998	2.65	15
12.370	IS3 1,4-Dichlorobenzene-D4	m/z150 (Semi Automatic)	IS	IS	IS
12.390	Benzene, 1,3-dichloro-	m/z146 (Semi Automatic)	0.998	2.75	12
12.525	Benzene, butyl-	m/z91 (Semi Automatic)	0.998	1.45	45
12.577	Benzene, 1,2-dichloro-	m/z146 (Semi Automatic)	0.998	1.84	19
13.185	Propane, 1,2-dibromo-3-chloro-	m/z157 (Semi Automatic)	0.996	15.58	61
13.258	Benzene, 1,2,3-trichloro-	m/z180 (Semi Automatic)	0.997	12.86	30
13.885	1,3-Butadiene, 1,1,2,3,4,4-hexachloro-	m/z225 (Semi Automatic)	0.998	10.19	62
13.975	Naphthalene	m/z128 (Semi Automatic)	0.993	4.86	12
14.148	Benzene, 1,2,4-trichloro-	m/z180 (Semi Automatic)	0.998	10.83	13

Table 2: List of analyzed VOCs and extrapolated MDLs (3x noise level)

Some of the compounds that EPA requires to keep under control are very volatile even at low temperature, such as the vinyl chloride that has a boiling point of -13.4°C. A solution containing only the very volatile compounds has been used to evaluate the repeatability of the injection (Table 3). The linearity was very good over the required concentration range with correlation coefficients > 0.995 for all the compounds as listed in Table 2.

Compound Name	Base Peak	Average Area	SD	RSD%
Methane, chloro-	m/z 50	13283.67	300.59	2.26
Ethene, chloro-	m/z 62	34586.67	2001.15	5.79
Methane, bromo-	m/z 94	12480.67	389.91	3.04
Ethyl Chloride	m/z 64	12825.67	389.91	3.04
Trichloromonofluoro methane	m/z 101	30880.00	1156.15	3.74

Table 3: Repeatability on 3 consecutive extraction of the most volatile compounds

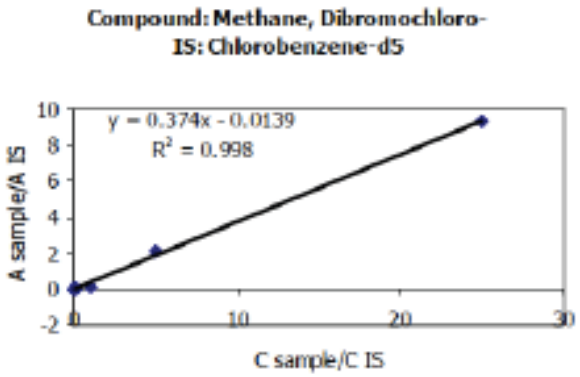


Figure 3: Example of Linearity response

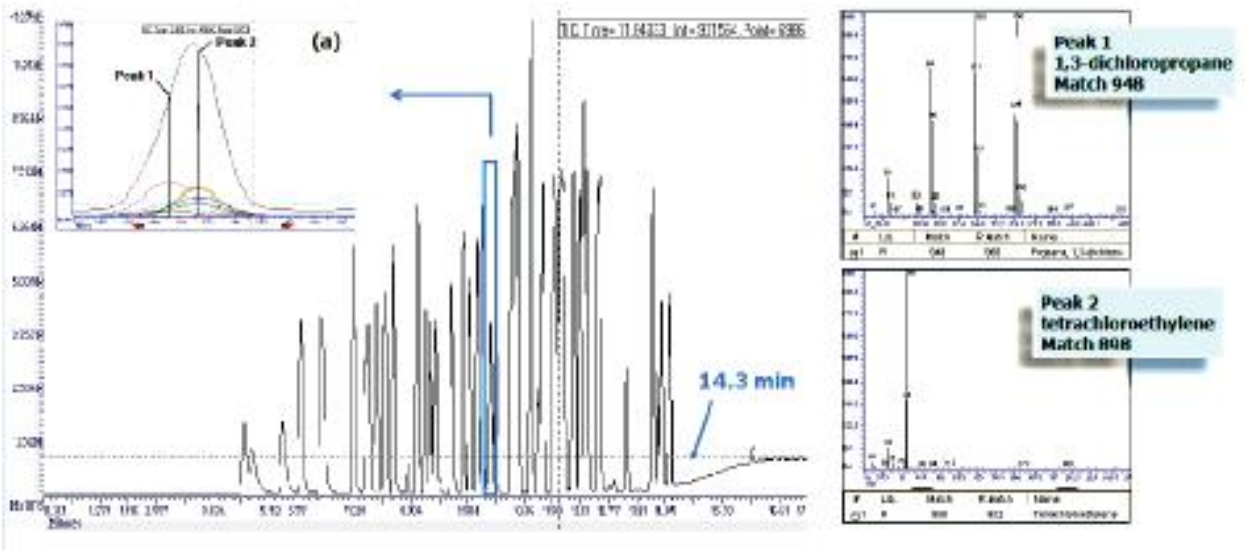


Figure 4 : Fast GC Chromatogram (TIC) of a 52 VOCs mixture and example of deconvolution elaboration (a)

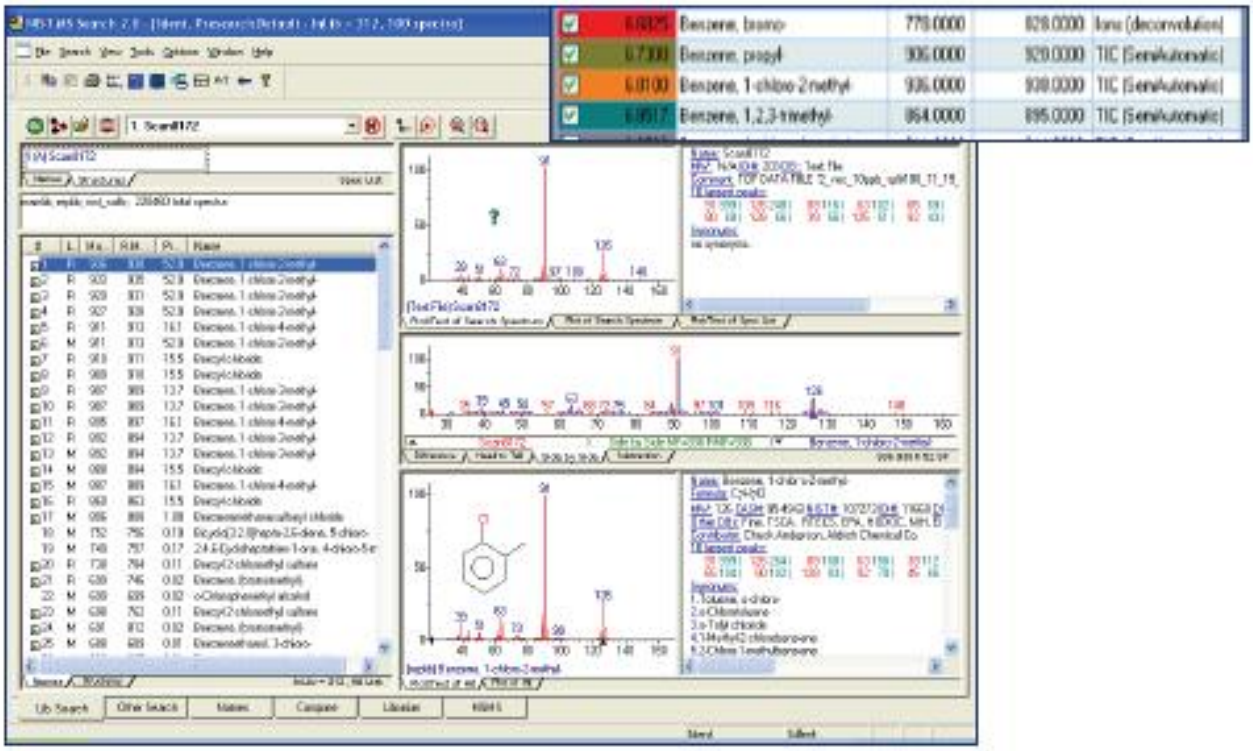


Figure 5 : Fast GC Chromatogram (TIC) of a 52 VOCs mixture and example of deconvolution elaboration (a)

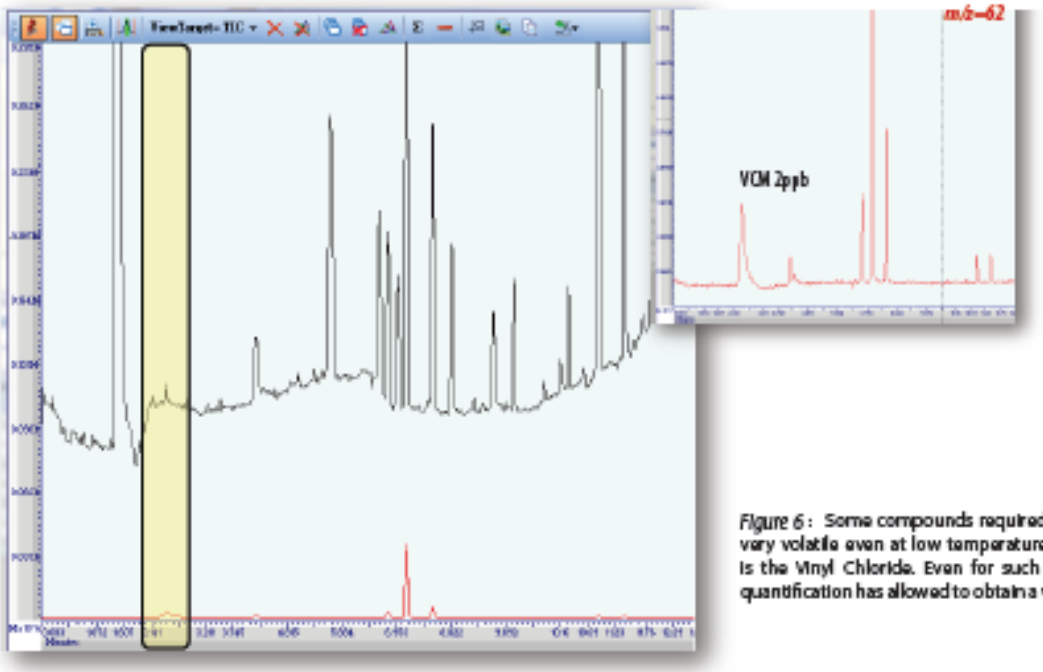


Figure 6: Some compounds required by the EPA norm are very volatile even at low temperature. Among these, there is the Vinyl Chloride. Even for such compound, a good quantification has allowed to obtain a very good peak shape.

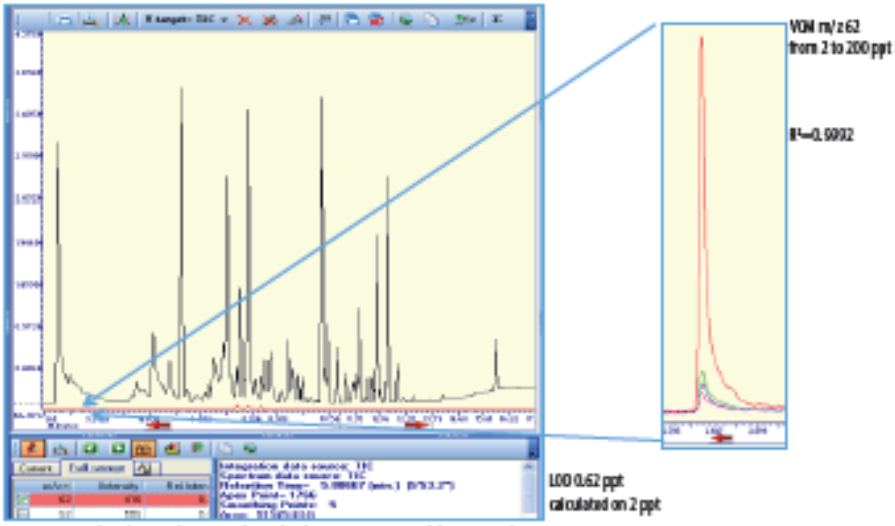
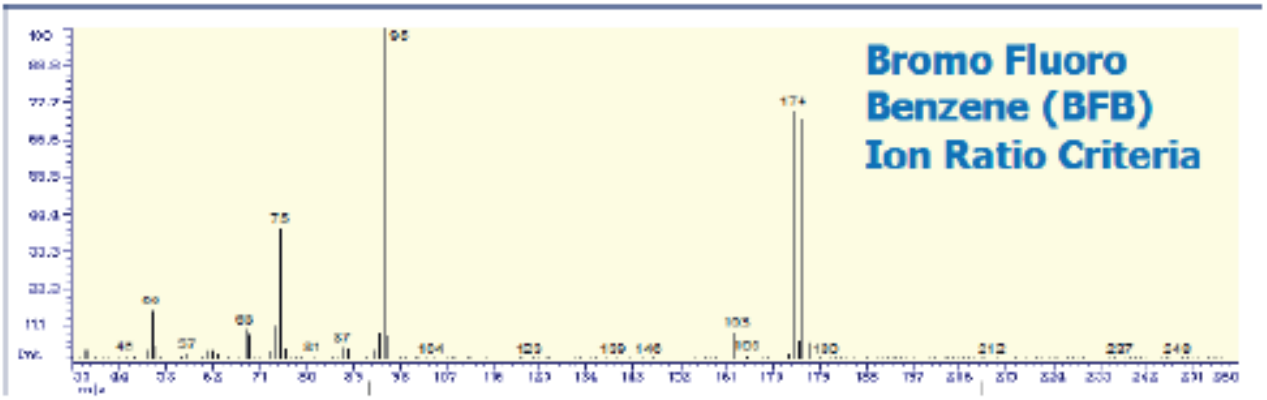


Figure 7: Thanks to the good peak shape, it is possible to easily calculate the calibration plot and obtain a very good minimum detectable level like 3 times the noise on the lower concentration of calibration (2 ppt)



Ion m/z	EPA 524 Ion Ratio Criteria	MasterTOF % Relative Intensity	Pass/Fail
50	15-40 % of mass 95	15.7	✓ PASS
75	30-60 % of mass 95	39.1	✓ PASS
95	Base peak	100	✓ PASS
96	5-9 % of mass 95	7.1	✓ PASS
173	< 2 % of mass 174	1.8	✓ PASS
174	> 50 % of mass 95	74.6	✓ PASS
175	5-9 % of mass 174	7.8	✓ PASS
176	95-105 % of mass 174	97.0	✓ PASS
177	5-10 % of mass 176	6.8	✓ PASS

Figure 8 : EPA method 524.3 requires to check the quality of fragmentation for the BFB. All the ion ratio criteria can be achieved with a standard tuning of the system without any specific tuning required.

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