APPLICATION NOTE

Gas Chromatography/
Mass Spectrometry

Author:

Maria Carola Salvi

PerkinElmer, Inc.
Milan, Italy

Determination of 1 ppt of 1,2,3-Trichloropropane and of 1,2-Dibromoethane in Groundwater

Introduction

For the protection of human health and the environment it is essential to avoid and prevent pollution of our water systems.

In this regard, the European Union directives assist the member states to define the activities to be programmed and the objectives to be achieved.

In this framework, the chemical analysis of the water system is the main activity to preserve the healthiness of the waterways through monitoring and detection of substances that are harmful to the environment and to the health of citizens.

The search for various pollutants in groundwater was carried out until 2006, pursuant to the M.D. 471 of 25/10/1999 (Regulation containing criteria, procedures and modalities for securing, reclaiming and restoring the environment in polluted areas, pursuant to Article 17 of the Legislative Decree of 5 February 1997, No. 22). Since May 2006, the Legislative Decree No. 152/06 entered into force which confirmed as detectability values for 1,2,3-trichloropropane and 1,2-dibromoethane concentrations equivalent to 0.001 µg/l. The purpose of this work is to demonstrate the achievement of these limits by means of a GC/MS system equipped with P&T (Figures 1).

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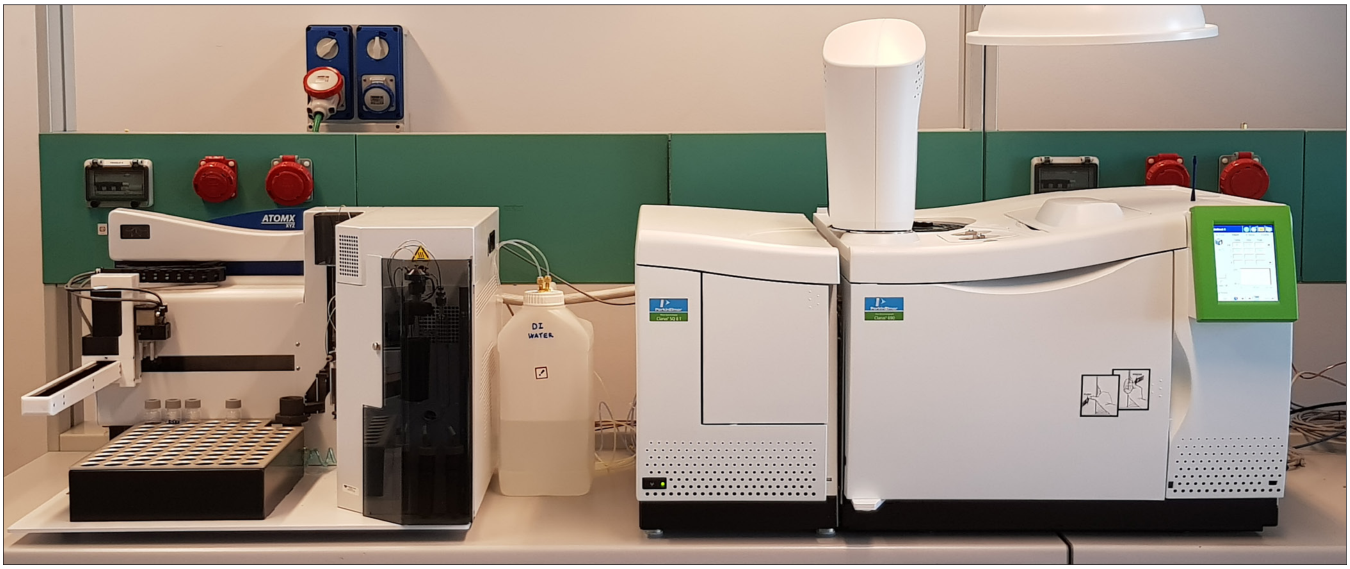


Figure 1. System P&T with Clarus SQ 8 GC/MS.

Conditions

For the analysis of trace VOCs to be successful, the environment in which the tests are carried out is of vital importance. Care must be taken to eliminate very low concentrations of the components of interest to avoid any likelihood of false positives.

In addition, where possible, it is recommended to keep the place dedicated to sample or standard preparation free of solvents or anything else that might interfere with the analysis while keeping the workplace clean and tidy.

Instruments

As a chromatographic system, the Clarus® 690 GC was used, equipped with a PSS injector that can be programmed in temperature, flow, pressure and velocity. The detector used is the SQ 8 mass spectrometer which is robust and easy to maintain. This analysis was done with an electronic impact source.

For the preparation, the Tekmar® Atomx XYZ® purge and trap (P&T) system was used to analyze, by pre-concentration, both soil and waters as well as the possible dilution of the sample. It can be automated by software and is able to add variable volumes of internal standards, surrogates and matrix spikes, while performing methanol extractions.

Experiment

The analyses were carried out both in Full Scan mode to obtain a qualitative recognition and in SIM to achieve maximum sensitivity, using specific ions for each component. An Elite-624Sil MS column 60 m, 0,32 mm 1,8 um (P/N N9315070) was used obtaining an excellent separation avoiding troublesome co-elutions, in compliance with the EPA 8260B method.

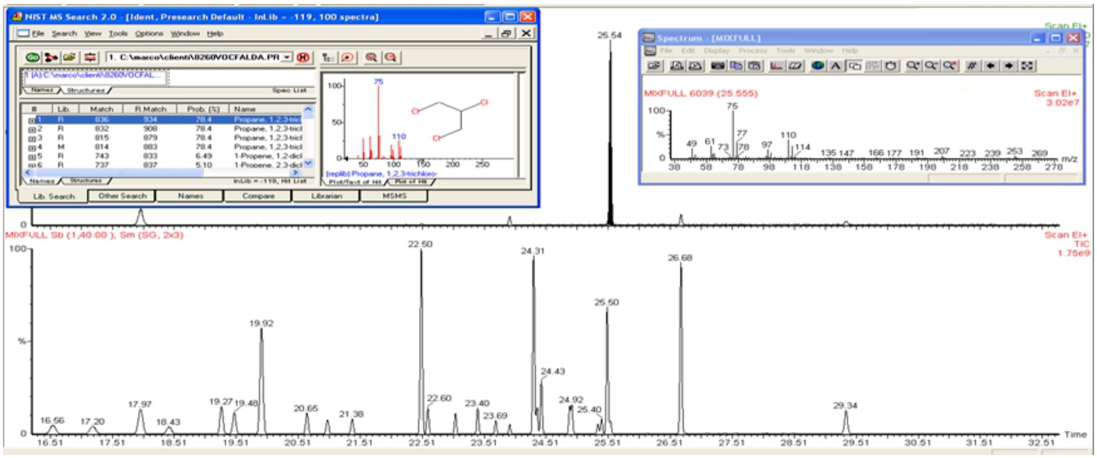
A gas flow, typically Helium or Nitrogen, is used in the P&T system. It is bubbled in a special 25 ml sparger in order to extract the volatile substances, concentrate them on the trap and subsequently desorb them directly into the GC/MS. Furthermore, for each specific instrumental parameter, values provided by Tekmar have been applied, all in accordance with the official EPA 5030B method.

Results

The chromatograms in the report below were obtained by analyzing samples prepared using the following procedure:

A known amount of concentrated standard was added to 25 ml of contaminant-free natural mineral water to reach the desired concentration levels of 0,001 µg/l.

Figures 2 and 3 show the traces obtained from a Full Scan acquisition of an aqueous solution containing 5 µg/l for each analyte. This concentration has allowed us, through the relative mass spectra, to recognize each component in the library.


NIST MS Search 2.0 - [Ident, Presearch Default - InLib = -119, 100 spectra]

1. C:\marco\clienti\8260VOCFALDA.PR

1 (A) C:\marco\clienti\8260VOCFAL...

#	Lib.	Match	R.Match	Prob. (%)	Name
1	R	836	934	78.4	Propane, 1,2,3-tricl
2	R	832	908	78.4	Propane, 1,2,3-tricl
3	R	815	879	78.4	Propane, 1,2,3-tricl
4	M	814	883	78.4	Propane, 1,2,3-tricl
5	R	743	833	6.49	1-Propene, 1,2-dicl
6	R	737	837	5.10	1-Propene, 2,3-dicl

InLib = -119, Hit List

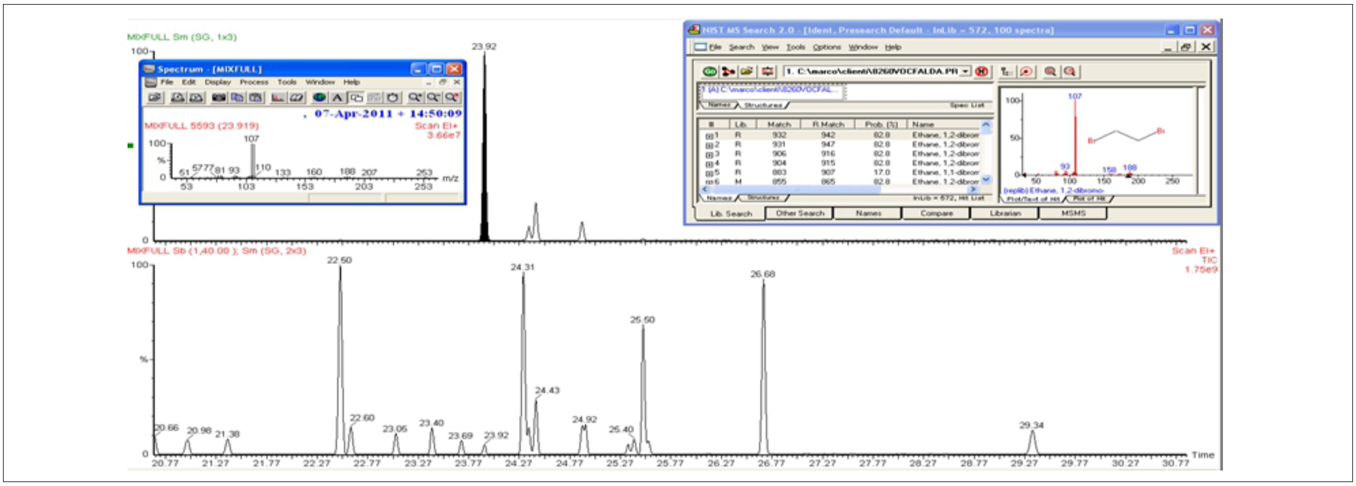
(replib) Propane, 1,2,3-trichloro-

Spectrum - [MIXFULL]

MIXFULL 6039 (25.555) Scan EI+ 3.02e7

MIXFULL Sb (1,40.00); Sm (SG, 2x3) Scan EI+ TIC 1.75e9

Figure 2. 1,2,3, Trichloropropane recognition.



#	Lib.	Match	R.Match	Prob. (%)	Name
1	R	932	942	82.8	Ethane, 1,2-dibrom
2	R	931	947	82.8	Ethane, 1,2-dibrom
3	R	906	916	82.8	Ethane, 1,2-dibrom
4	R	904	915	82.8	Ethane, 1,2-dibrom
5	R	883	907	17.0	Ethane, 1,1-dibrom
6	M	855	865	82.8	Ethane, 1,2-dibrom

Figure 3. 1,2-Dibromoethane recognition.

Figures 4 and 5 show the two chromatograms obtained by concentrating a solution containing respectively 0.001 µg/l of 1,2-Dibromoethane and 1,2,3-Trichloropropane to prove the effectiveness of the method in reaching the limits required by law. In this case the signal has been acquired in SIM, so as to obtain maximum instrumental sensitivity.

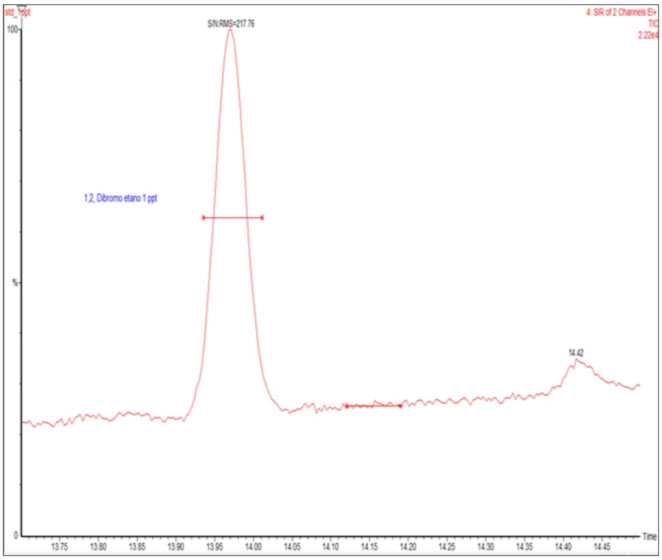


Figure 4. 1,2-Dibromoethan.

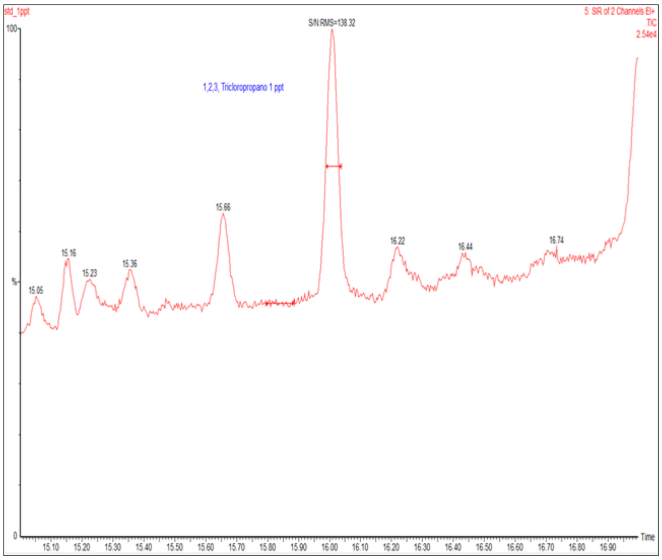


Figure 5. 1,2,3-Trichloropropane.

Below are the calculated signal/noise ratio values, which show the possibility of carrying out a quantitative analysis, both being higher than 10.

1,2,3-Trichloropropane = 14.08

1,2-Dibromoethane = 20.32

As a further feasibility test, in Figures 6 and 7 a comparison between a standard at 0.001 µg/l and the water used as a matrix for its preparation is reported.

Moreover the water sample has been analyzed after injecting a 50 µg/l standard to proove the absence of any carry-over in the system.

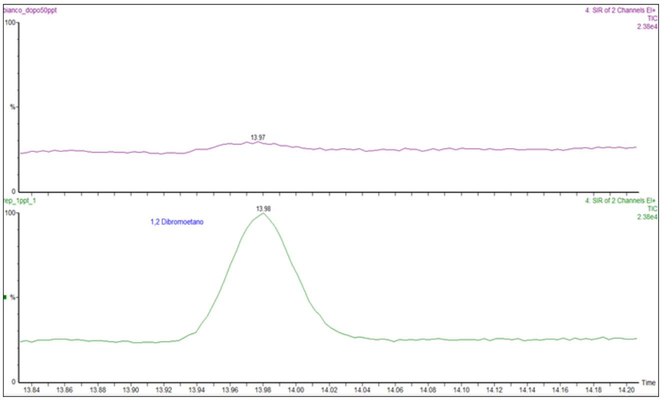


Figure 6. 1,2-Dibromoethane.

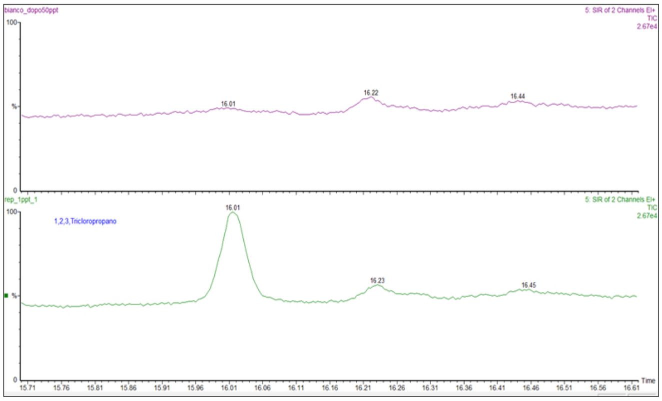


Figure 7. 1,2,3-Trichloropropane.

Finally, the calibration curves were created (Figures 8 and 9) replicating each level and including the origin. The concentration levels used are provided as follows:

Level 1: 0.001 µg/l
Level 2: 0.005 µg/l
Level 3: 0.010 µg/l
Level 4: 0.050 µg/l

In both curves, correlation coefficients higher than 0.995 were obtained in order to respect the most common validation standards.

Table 1 shows the retention times, areas and concentrations for five replicates performed at both concentration levels equal to 1 ng/l, and 10 ng/l plus a blank solution with no contaminants.

Conclusions

This analysis proves it is possible to achieve the most restrictive analytical parameters, such as European legislation, without the use of refocusing systems and avoiding the use of cryogenic liquids. In this way, the cost of analysis is reduced, simplified and avoids the use of potentially dangerous substances. Throughput and productivity of the system are also improved by the Clarus SQ 8 GC/MS with a fast-cooling GC oven.

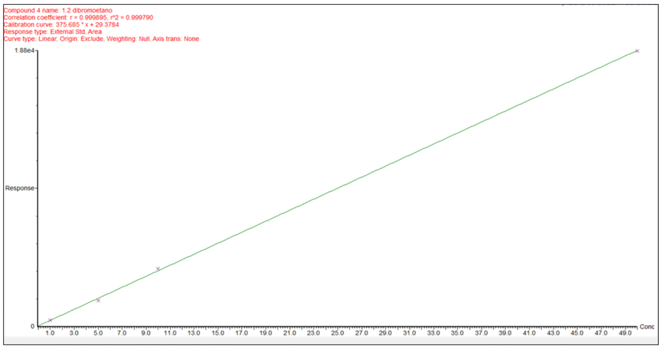


Figure 8. Calibration curve 1,2-Dibromoethane.

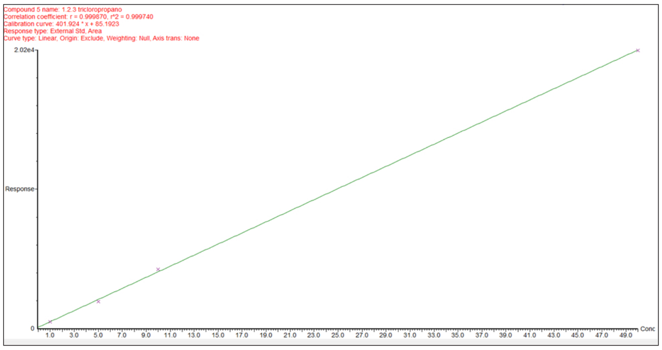


Figure 9. Calibration curve 1,2,3-Trichloropropane.

Table 1. Data summary table for low and high concentration of the most challenging chemicals.

	1,2 Dibromoetano			1,2,3 Tricloropropano		
	RT Min	**AREA**	**Conc. ng/l (ppt)**	**RT Min**	**AREA**	**Conc. ng/l (ppt)**
Blank solution (Used as Standard Matrix)	13,97	34,46	0,01	16,00	42,88	0,00
Rep_1,00 ng/l _1	13,98	450,13	1,12	16,01	511,36	1,06
Rep_1,00 ng/l _2	13,98	443,23	1,10	16,01	534,16	1,12
Rep_1,00 ng/l _3	13,97	452,93	1,13	16,01	525,37	1,10
Rep_1,00 ng/l _4	13,97	451,24	1,12	16,01	520,35	1,08
Rep_1,00 ng/l _5	13,98	446,56	1,11	16,01	532,00	1,11
Media	13,98	448,82	1,12	16,01	524,65	1,09
CV%	0,03	0,78	0,91	0,01	1,57	1,97
	1,2 Dibromoetano			**1,2,3 Tricloropropano**		
	RT Min	**AREA**	**Conc. ng/l (ppt)**	**RT Min**	**AREA**	**Conc. ng/l (ppt)**
Rep_10,00 ng/l _1	13,97	4.034,41	10,66	16,01	4.364,55	10,65
Rep_10,00 ng/l _2	13,97	4.150,41	10,97	16,01	4.490,40	10,96
Rep_10,00 ng/l _3	13,97	4.160,20	11,07	16,00	4.502,50	10,99
Rep_10,00 ng/l _4	13,98	4.186,81	11,07	16,01	4.454,81	10,87
Rep_10,00 ng/l _5	13,98	4.417,46	11,68	16,01	4.724,54	11,54
Media	13,97	4.189,86	11,08	16,01	4.507,36	11,00
CV%	0,02	3,34	3,36	0,02	2,95	2,99

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

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