TECHNICAL NOTE 73762

Analysis of VOCs in wastewater using P&T-single quadrupole GC-MS

Authors: Adam Ladak[1], Terry Jeffers[1], David Lee[2], and Amy Nutter[3]

[1]Thermo Fisher Scientific, USA
[2]Thermo Fisher Scientific, Runcorn, UK
[3]Teledyne Tekmar, Mason, OH, USA

Keywords: EPA, VOCs, environmental, trace analysis, gas chromatography, single quadrupole mass spectrometry, selected ion monitoring, environmental testing lab, environmental sample analysis, contract testing labs, wastewater, purge and trap

Goal

Show proof of principle for the major method challenges of U.S. EPA Method 624 for the quantitation of volatile organic compounds (VOCs) in wastewater, using the Teledyne Tekmar Atomx XYZ purge and trap (P&T) system along with a Thermo Scientific™ ISQ™ 7000 Mass Spectrometry (MS) system coupled with a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC) and Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS). Linearity, method detection limit (MDL), precision, accuracy, and Initial Demonstration of Capability (IDC) were assessed to evaluate method performance.

Introduction

It is crucial that environmental analytical testing laboratories monitor wastewater for the presence of volatile organic compounds (VOCs). U.S. EPA Method 624 is used in environmental labs to test wastewater to ensure that it does not contain any pollutants and complies with the Clean Water Act.[1] If VOCs are released into wastewater from industrial activities, they can have an adverse effect on plants, wildlife, and ultimately the public.[2] It is extremely important that analytical testing labs ensure accurate detection and quantitation of VOCs to verify if wastewater samples are not contaminated. Due to technological advances in analytical instrumentation and techniques, EPA Method 624 allows the analyst to modify P&T parameters and GC-MS conditions. This can result in reduced sample run time and increased laboratory throughput in a 12-hour period.

To perform EPA Method 624, method acceptance criteria must be achieved. These criteria include creating a working calibration curve, MDL and IDC accuracy, and precision for target compounds. As the sample matrix is water, it is essential that moisture is not introduced into the analytical column as this could damage the column and affect the results.

The following evaluation describes the use of the ISQ 7000 MS system coupled to the Atomx XYZ P&T for the main criteria of U.S. EPA Method 624.

Experimental

Sample preparation

A working 50 ppm calibration standard was prepared in methanol from Restek™ standards: 624 Calibration Mix #1 and Volatiles MegaMix™ Standard, EPA Method 624. In total, the standard contained 31 compounds.

The calibration curve was prepared from 0.5 to 200 parts per billion (ppb) (µg/L) for all compounds. The relative response factor (RRF) was calculated for each compound using one of the three internal standards: bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane. Surrogate standards consisted of pentafluorobenzene, fluorobenzene, and 1-bromo-4-fluorobenzene. Internal and surrogate standards were prepared together in methanol from Restek standards at a concentration of 30 parts per million (ppm) (mg/L), after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 30 ppb.

Seven 0.5 ppb standards were prepared for MDLs and precision calculations. Also, five 5 ppb standards were prepared for the IDC precision and accuracy calculations. All calibration, MDL, and IDC samples were analyzed with the Atomx XYZ conditions in Table 1.

Table 1. Tekmar Atomx XYZ water method parameters

Purge	Variable
Valve oven temp.	140 °C
Transfer line temp.	140 °C
Sample mount temp.	90 °C
Water heater temp.	90 °C
Sample vial temp.Temp	20 °C
Soil valve temp.	100 °C
Standby flow	10 mL/min
Condensate ready temp.	45 °C
Purge ready temp.	40 °C
Purge	Variable
Sample equilibrate time	0.00 min
Pre-sweep time	0.25 min
Prime sample fill volume	3.00 mL
Sample volume	5.00 mL
Sweep sample time	0.25 min
Sweep sample flow	100 mL/min
Sparge vessel heater	Off
Sparge vessel temp.	20 °C
Pre-purge time	0.00 min
Pre-purge flow	0 mL/min
Purge time	11.00 min
Purge flow	40 mL/min
Purge temp.	20 °C
Condensate purge temp.	20 °C
Dry purge time	0.00 min
Dry purge flow	100 mL/min

Desorb	Variable
Methanol needle rinse	Off
Methanol needle rinse volume	0.00 mL
Water needle rinse volume	7.00 mL
Sweep needle time	0.25 min
Dry purge temp.	20 °C
Desorb preheat temp.	245 °C
GC start signal	Begin Desorb
Desorb time	2.00 min
Drain flow	300 mL/min
Desorb temp.	250 °C
Bake	Variable
Methanol glass rinse	Off
Number of methanol glass rinses	0
Methanol glass rinse volume	0.00 mL
Water bake rinses	1
Water bBake rinse volume	7.00 mL
Bake rinse sweep time	0.25 min
Bake rinse sweep flow	100 mL/min
Bake rinse drain time	0.40 min
Bake time	2.00 min
Bake flow	200 mL/min
Bake temp.	260 °C
Condensate bake temp.	200 °C
Trap	#9
Purge gas	Nitrogen

GC-MS parameters

A TRACE 1310 GC was coupled to the ISQ 7000 MS system equipped with the Thermo Scientific™ NeverVent™ vacuum probe interlock (VPI) and a Thermo Scientific™ ExtractaBrite™ ion source. A Thermo Scientific™ TraceGOLD™ TG-VMS 20 m x 0.18 mm, 1 µm film (P/N 26080-4950) was used for compound separation. The GC run time is under 15 minutes and a 50 to 1 split injection was used. The ISQ 7000 MS system was operated in full-scan mode, which gave enough sensitivity to meet the regulatory requirements. Expanded method parameters for the GC-MS system are displayed in Table 2.

Table 2. GC-MS conditions

TRACE 1310 GC Conditions	
Column	TraceGOLD VMS, 20 m × 0.18 mm, 1 µm film Carrier gas: helium @ 1 mL/min Helium – 0.8 mL/min
Oven temperature program	35 °C, 3 min, 12 °C/min to 85 °C 25 °C/min to 225 °C, 2 min hold Run time: 14.767 min
Inlet	SSL at 200 °C, 50:1 split Purge flow: 0.5 mL/min
ISQ 7000 MS Conditions	
Temperature	Transfer line: 230 °C Ion source: 280 °C
Scan	Range: 35 amu to 260 amu Ionization mode: Electron ionization at 70 eV Solvent delay: 0.50 min Dwell/scan time: 0.15 s
Current	Emission current: 25 µA, Detector gain: 3.00E+005

Instrument control and data processing

Data were acquired, processed, and reported using Chromeleon CDS software, version 7.2. This software can control both the GC-MS system and the Tekmar Atomx XYZ P&T. This allows a single software to be utilized for the full workflow simplifying the instrument operation. Figure 1 shows the Chromeleon control of the Atomx XYZ P&T. The fully optimized method used within this application note is available for download via Thermo Scientific™ AppsLab. AppsLab contains all the parameters needed to acquire, process, and report the analytical data for EPA Method 624.2

Guided instrument setup of Atomx XYZ module within Chromeleon CDS

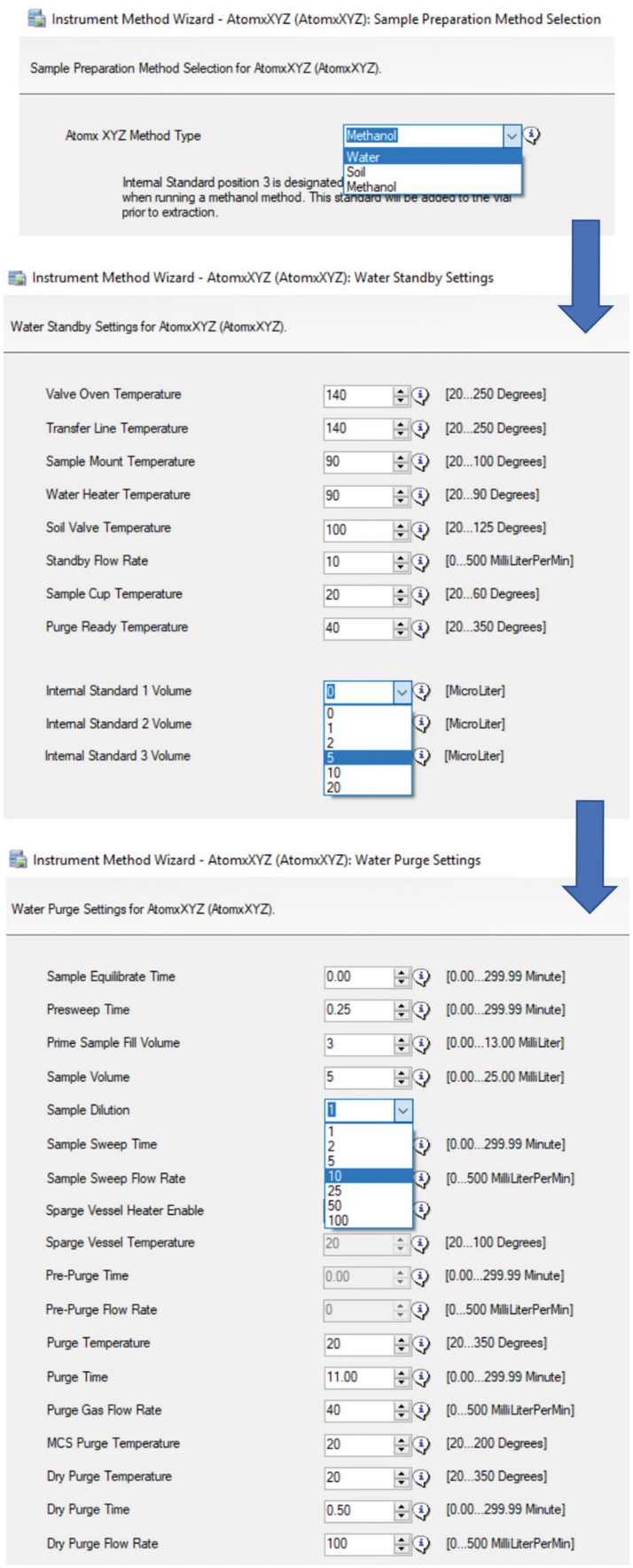

Figure 1. Chromeleon control of the Atomx XYZ P&T

Results and discussion

Chromatography

Excellent chromatography was achieved using the conditions described in Table 2. The moisture transferred onto the analytical column was minimized using the Atomx XYZ P&T, which limits any damage to the analytical column and increases method robustness. This is achieved by the moisture control system that improves water vapor removal from the samples. Figure 2 displays consistent peak shape and separation of a 10 ppb VOC standard with minimal water interference.

Linearity and sensitivity

A calibration range of 0.5–200 ppb was assessed for all compounds, except for chloroethane (2–200 ppb) and *cis*-1,3-dichloropropene (1–200 ppb). The calibration curves were used to calculate the average and relative standard deviation (%RSD) of the response factor (RF) for the calibration curve. The obtained values are shown in Table 3. To meet the EPA Method 624 criteria, the %RSD of the RF must be <35. The MDL was assessed using n=7 replicates of a 0.5 ppb standard for all compounds, except for *cis*-1,3-dichloropropene, which used n=7 replicates of a 1 ppb standard.

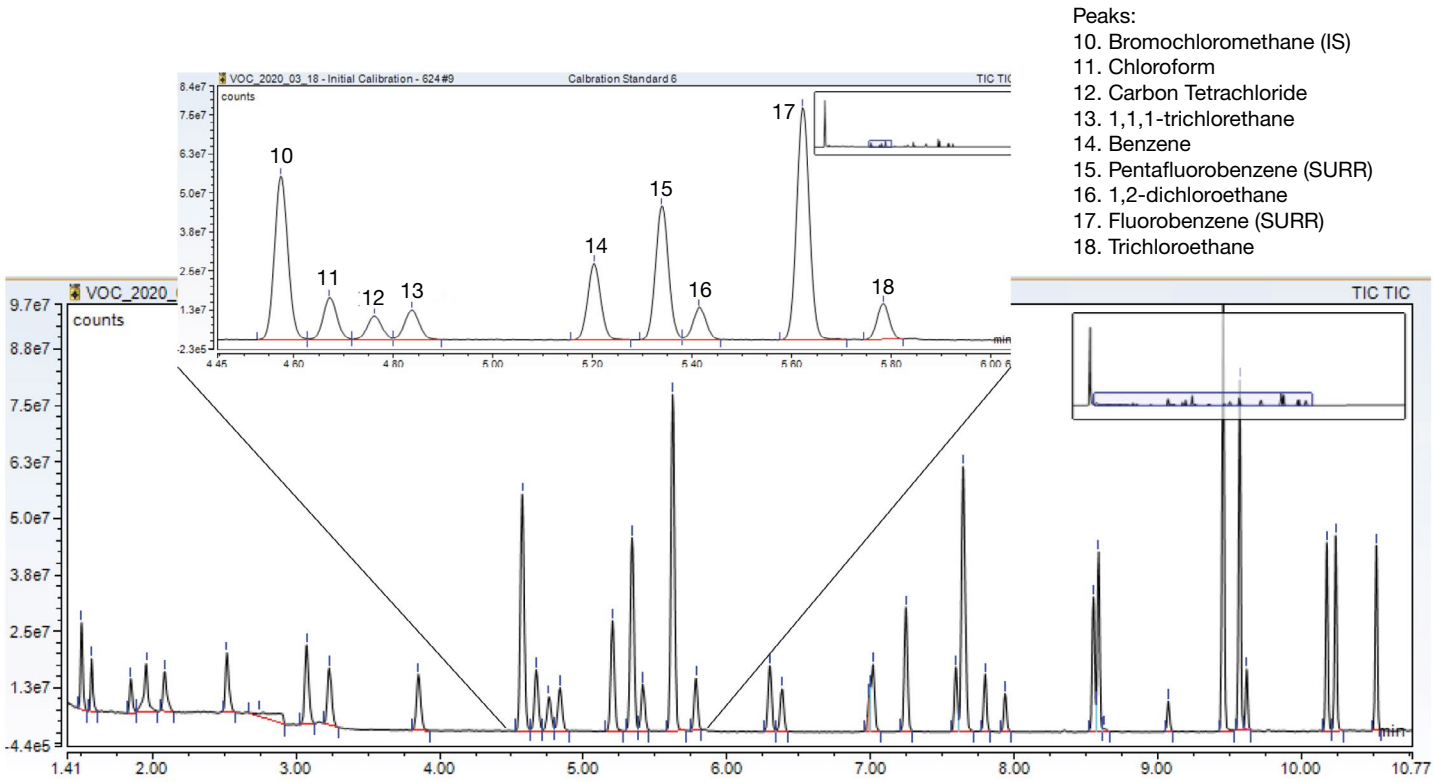

Figure 2. Total ion chromatogram (TIC) of a 10 ppb (equivalent to 10 µg/L in sample) VOC standard with an inset indicating consistent peak shapes and separation with minimal water interference

Table 3. Calibration results showing average and relative standard deviation (%RSD) of the response factor (RF) for each compound

Peak name	Retention time	Quantitation ion	Linearity (RF %RSD)	Average RF
Chloromethane	1.51	50	17.8	1.4
Vinyl chloride	1.58	62	5.61	0.7
Bromomethane	1.85	94	16.7	0.3
Chloroethane	1.96	64	16.2	0.4
Trichlorofluoromethane	2.09	101	5.76	0.6
1,1-Dichloroethene	2.52	96	6.09	0.4
Methylene chloride	3.07	84	14.5	0.6
trans-1,2-Dichloroethene	3.22	96	5.83	0.4
1,1-Dichloroethane	3.84	63	5.41	1.1
Bromochloromethane (ISTD)	4.57	49		
Chloroform	4.67	83	6.42	0.8
Carbon tetrachloride	4.76	117	13.7	1.7
1,1,1-Trichloroethane	4.83	97	8.67	2.2
Benzene	5.20	78	6.55	7.2
Pentafluorobenzene (surr)	5.34	168	8.64	3.8
1,2-Dichloroethane	5.41	98	13.9	0.2
Fluorobenzene (surr)	5.62	96	1.75	7.4
Trichloroethene	5.78	130	10.2	1.4
1,2-Dichloropropane	6.29	112	10.1	0.2
Bromodichloromethane	6.38	127	9.20	0.2
2-Chloroethyl vinyl ether	6.99	106	3.90	0.2
trans-1,3-Dichloropropene	7.02	75	10.4	2.7
Toluene	7.24	92	7.18	3.8
Tetrachloroethylene	7.59	164	6.07	0.3
2-Bromo-1-chloropropane (ISTD)	7.64	79		
cis-1,3-Dichloropropene	7.65	75	17.7	0.7
1,1,2-Trichloroethane	7.80	97	9.54	0.3
Dibromochloromethane	7.93	127	12.2	0.3
Chlorobenzene	8.55	112	8.35	1.1
Ethylbenzene	8.58	106	6.55	0.6
Bromoform	9.07	173	7.80	0.3
4-Bromofluorobenzene (surr)	9.45	95	4.37	0.8
1,4-Dichlorobutane (ISTD)	9.57	55		
1,1,2,2-Tetrachloroethane	9.61	168	9.60	0.0
1,3-Dichlorobenzene	10.17	146	10.9	1.2
1,4-Dichlorobenzene	10.24	146	10.7	1.2
1,2-Dichlorobenzene	10.52	146	10.0	1.2

1. Calibration curve 2–200 ppb (µg/L)
2. Calibration curve 1–200 ppb (µg/L)
3. IDL calculated from n=x repeat injections of a 1 ppb (µg/L) standard

Table 4 displays the MDL values, which are <0.25 ppb for most compounds, and the precision data obtained at the MDL level, which shows %RSD of calculated amount <20 for all compounds. Table 4 also displays the IDC results for all compounds. Using n=5 replicates of a 5 ppb standard, accuracy and precision were assessed.

Table 4. Method detection limits and initial demonstration of capability results

	Method detection limit (n=7, 0.5 ppb)			Initial demonstration of capability (n=5, 5 ppb)	
Peak name	**Average conc.**	**MDL**	**Precision (<20%)**	**Precision (<20%)**	**Accuracy (70–110%)**
Chloromethane	0.54	0.31	18.4	6.0	75
Vinyl chloride	0.43	0.12	8.9	8.6	79
Bromomethane	0.69	0.17	7.6	5.7	90
Chloroethane	0.68	0.28	12.9	6.9	105
Trichlorofluoromethane	0.44	0.15	10.9	7.6	79
1,1-Dichloroethene	0.44	0.11	8.0	7.7	82
Methylene chloride	0.56	0.09	5.0	2.2	88
trans-1,2-Dichloroethene	0.50	0.12	7.3	6.4	87
1,1-Dichloroethane	0.45	0.09	6.1	4.3	87
Bromochloromethane (ISTD)					
Chloroform	0.44	0.08	6.0	3.6	88
Carbon tetrachloride	0.38	0.09	7.7	7.2	87
1,1,1-Trichloroethane	0.41	0.11	8.3	6.2	87
Benzene	0.44	0.09	6.7	3.8	85
Pentafluorobenzene (surr)	30.0		2.2	1.9	97
1,2-Dichloroethane	0.60	0.29	15.4	1.3	96
Fluorobenzene (surr)	29.8		1.0	0.9	99
Trichloroethene	0.44	0.12	8.5	6.2	86
1,2-Dichloropropane	0.50	0.21	13.1	9.4	83
Bromodichloromethane	0.42	0.18	13.7	6.2	91
2-Chloroethyl vinyl ether	0.46	0.17	11.8	1.1	87
trans-1,3-Dichloropropene	0.40	0.10	7.8	1.9	81
Toluene	0.45	0.12	8.4	5.0	84
Tetrachloroethylene	0.44	0.13	9.7	5.9	77
2-Bromo-1-chloropropane (ISTD)					
cis-1,3-Dichloropropene	1.2	0.22	5.7	3.0	77
1,1,2-Trichloroethane	0.43	0.07	4.9	3.5	85
Dibromochloromethane	0.41	0.09	6.7	2.1	82
Chlorobenzene	0.45	0.10	7.0	2.9	80
Ethylbenzene	0.42	0.12	9.1	5.1	76
Bromoform	0.41	0.07	5.3	1.9	78
4-Bromofluorobenzene (surr)	28.5		2.2	2.5	95
1,4-Dichlorobutane (ISTD)					
1,1,2,2-Tetrachloroethane	0.47	0.18	11.9	2.3	85
1,3-Dichlorobenzene	0.50	0.14	9.0	2.5	79
1,4-Dichlorobenzene	0.51	0.13	8.1	3.0	80
1,2-Dichlorobenzene	0.48	0.13	8.5	2.3	82

To validate the quality control of the calibration curve, this IDC procedure must be completed and continuing calibration checks must be performed with samples to ensure data quality. To meet the IDC criteria the %RSD of the calculated results must be <20 and the accuracy must be within 70–100%. Figure 3 demonstrates the quantitation of 1,1-dichloroethane in the 0.5 ppb standard with excellent library spectral matching and calibration curve.

Conclusion

The combined solution of the TRACE 1310 GC coupled with the ISQ 7000 system and the Atomx XYZ P&T system provides guidance to achieving EPA Method 624 criteria. The Atomx XYZ concentrator's efficient trap cooling design reduces sample cycle time and enables an increase in sample throughput. The moisture control system improves water vapor removal, thereby reducing peak interference and increasing GC column life span. The ISQ 7000 VPI and ExtractaBrite ion source allow users to exchange ionization sources and analytical columns without venting the instrument significantly, reducing instrument downtime and minimizing sample analysis interruptions. Combined, these technologies effectively address the challenges of analytical testing laboratories for the analysis of VOCs and provide a robust, sensitive solution needed for ensuring maximized instrument output and regulatory method compliance.

- The ISQ 7000 VPI GC-MS coupled with the Tekmar Atomx XYZ P&T exceeds all the requirements outlined in EPA Method 624 for analysis of VOCs in wastewater.
- MDLs calculated from n=7 0.5 ppb standards showed no interference from excessive water and resulted in values <0.25 ppb for most compounds.
- Precision and accuracy for n=5 5 ppb standards showed excellent results with %RSD <20% and recovery values between 75% and 105%.

Further information on VOC analysis using the ISQ 7000 GC-MS system and the Atomx XYZ P&T can be found in the Thermo Scientific AppsLab library.[3]

References

1. United States Environmental Protection Agency, Summary of the Clean Water Act. https://www.epa.gov/laws-regulations/summary-clean-water-act
2. United States Environmental Protection Agency, Guideline Series, Control of Volatile Organic Compound Emissions from Industrial Wastewater. https://www3.epa.gov/airquality/ctg_act/199209_voc_epa453_d-93-056_industrial_wastewater(draft).pdf
3. Thermo Scientific AppsLab Library. https://appslab.thermofisher.com/

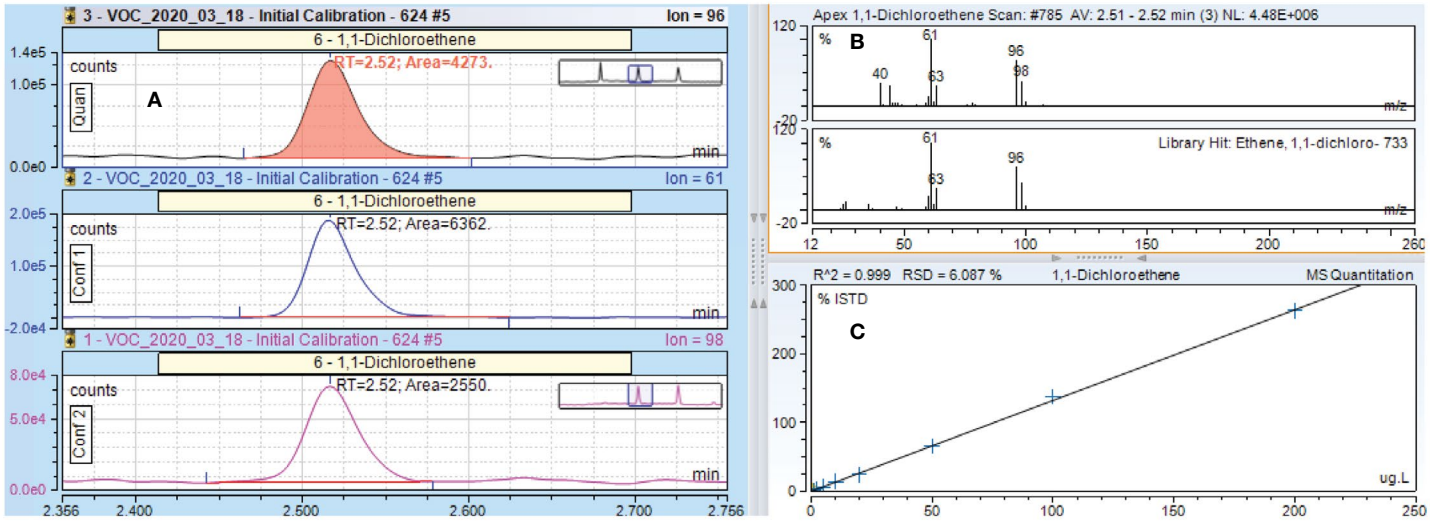

Figure 3. Chromeleon results browser showing extracted ion chromatograms for 1,1-dichloroethene in the 0.5 ppb standard, quantitation ion and two confirming ions (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 0.5 ppb to 200 ppb (C)

Find out more at **thermofisher.com**

© 2020 Thermo Fisher Scientific Inc. All rights reserved. Restek trademarks are the property of Restek Corporation. Atomx XYZ is a trademark of Teledyne Tekmar. All other trademarks are the property of Thermo Fisher Scientific and its subsidiaries. This information is presented as an example of the capabilities of Thermo Fisher Scientific Inc. products. It is not intended to encourage use of these products in any manners that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details. **TN73762-EN 0920S**

ThermoFisher SCIENTIFIC