

# Analysis of Haloacetic Acids and Dalapon in Water by GC-MS Using TraceGOLD™ TG-5MS with SafeGuard GC Column

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## Abstract

The performance and suitability of using an ultra low bleed silylene stationary phase (similar to 5 % phenyl methylpolysiloxane) GC column with an integrated guard column is evaluated for the identification of haloacetic acids and dalapon in water. This method can provide a confirmational identification using EPA method 552.2

## Introduction

US EPA method 552 is an analytical method used for determining the presence of haloacetic acids (HAA) and dalapon (an acidic herbicide) in drinking water. The US EPA method 552.2 usually involves a liquid-liquid extraction step followed by derivatization of analytes. This analysis is usually performed using an electron capture detector (ECD) which is selective towards halogenated compound. However, in this case an alternative detector, a mass spectrometer was used to determine HAA and dalapon at 250 ppb in water in SIM mode.

The analysis of HAA and dalapon according to the EPA method 552 was performed on a TRACE™ GC coupled to a Thermo Scientific single quadrupole ISQ mass spectrometer.

The analytical column selected for this analysis was a Thermo Scientific ultra low bleed phase TraceGOLD TG-5SiIMS with SafeGuard column. This column chemistry is equivalent to that specified in the EPA method 552.2. The SafeGuard format is a continuous length of phased analytical column (similar to 5 % phenyl methylpolysiloxane) with an un-phased integrated guard column. The SafeGuard column protects the analytical column from degradation when harsh derivatization reagents are used and thereby extends the lifetime of the analytical column. This column format eliminates the potential for leaks at the point of connection and makes it desirable for use with a mass spectrometer.

The suitability and the performance of this method was demonstrated using a TraceGOLD™ TG-5SiIMS 30m x 0.25 mm x 0.25 µm GC column with 10 m SafeGuard.



## Experimental Details

Consumables		Part Number
Column:	TraceGOLD TG-5SiIMS 30 m x 0.25 mm x 0.25 µm (with 10m SafeGuard)	26096-1421
Septum:	BTO, 17 mm	31303211
Liner:	FOCUS Splitless liner, 5 x 8 mm	45350033
Column ferrules:	100% Graphite ferrules for TRACE injector 0.1-0.25 mm ID	29053488
Column ferrules:	Graphite/vespel for transfer line 0.1-0.25mm ID	29033496
Injection syringe:	10 µL Fixed needle syringe for a TriPlus Autosampler	36500525
	Thermo Scientific Chromacol 9mm screw 0.3mL fixed insert amber Micro+ vials	03-FISV (A)
	Thermo Scientific Chromacol 9mm screw caps with Silicone/PTFE septa	9-SC(B)-ST101

Sample Handling Equipment		Part Number
	Thermo Scientific Reacti-Therm III Heating/stirring Module	TS-18823
	Thermo Scientific Reacti-Vap III Evaporator	TS-18826
	Thermo Scientific Reacti-Vap block	TS-18814
	Thermo Scientific Reacti-Vial reaction vials 10 mL	TS-13225
	Thermo Scientific 2 mL amber vial and screw tops	60180-565

Chemicals and Reagents		Part Number
	Fisher Scientific HPLC grade Methyl tert-butyl ether (MTBE)	M/4496/17
	Fisher Scientific HPLC grade water	W/0106/17
	Fisher Scientific HPLC grade Methanol	M/4056/17
	Fisher Scientific HPLC grade Sulfuric acid	S/9220/PB08

## Key Words

- TraceGOLD TG-5SiIMS with SafeGuard
- Haloacetic acids (HAA)
- Dalapon
- Liquid-liquid extraction
- Derivatization
- EPA method 552
- Guard Column

## Sample Preparation

**Extraction:** 2 mg of ammonium chloride was added to 20 mL water. The solution was spiked with 10 µg/mL and 250 ng/mL of dalapon and HAAs listed in Table 1 in water. The pH of the solution was then adjusted to less than 0.5 with concentrated sulfuric acid followed by an immediate addition of 8 g of sodium sulfate. 2 mL of methyl tert-butyl ether (MTBE) was then added and phase separation was allowed.

**Derivatization:** Approximately 1.5 mL of the MTBE layer was transferred to a Reacti-vial containing a magnetic stirrer followed by the addition of 0.5 mL of 10% sulfuric acid/methanol. The Reacti-vial was capped and placed in the Reacti-therm for 2.5 hours at 50 °C. The reaction was quenched with 2 x 1 mL of saturated sodium bicarbonate and after phase separation, a 500 µL of aliquot was transferred to 2mL vial.

## Separation Conditions

Instrumentation:	Thermo Scientific TRACE GC Ultra
Carrier gas:	Helium
Split flow:	10 mL/minute
Column flow:	1.2 mL/minute, Constant flow
Oven temperature:	40 °C (1 minute), 5 °C/minute, 135 °C (1 minute)

Injector type:	Split/Splitless
Injector mode:	Split
Split ratio:	10:1
Injector temperature:	220 °C

## MS Conditions

Instrumentation:	Thermo Scientific ISQ GC Single Quadrupole Mass Spectrometer
Transfer line temperature:	260 °C
Source temperature:	230 °C
Ionization conditions:	EI
Electron energy:	70 eV
Solvent delay:	3.2 min
Scan range:	35-300 amu full scan dwell time 0.25 second

## Injection Conditions

Instrumentation:	Thermo Scientific TriPlus Autosampler
Injection Volume:	2 µL
Pre and Post Injection Dwell Time:	5 seconds

## Data Processing

Software:	Thermo Scientific XCaliburTM
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## Results

The separation of HAAs and dalapon in water was achieved using a TG-5SilMS with SafeGuard GC column (Figure 1). Extraction and derivatization of the HAA and dalapon in water was performed following EPA method 552.2. MS analysis was performed in SIM and  $m/z$  59 was used for peak identification. This ion is commonly found in the derivatized forms of HAA and dalapon.

Peak tailing can often be observed when derivatized strong acids interact with a low polarity chromatographic GC column. This low bleed stationary phase (TraceGOLD TG-5SilMS) incorporates phenyl groups into the polymer backbone, which gives an outstanding inertness to derivatized strong acids. In addition, the integrated guard column (SafeGuard) refocuses analytes onto the stationary phase of the analytical column, giving a sharper peak shapes and improved sensitivity to analytes of <250 ng/mL. The SIM chromatogram of HAA and dalapon at 250 ng/mL is shown in Figure 2.

The components identified with their retention times is displayed in Table 2. Three sample extractions and derivatization of HAA and dalapon in water were performed at 250 ng/mL concentration level. No internal standard was added and relative standard deviation was determined based on the peak areas of the analytes. This was found to be in the range of 8-18%.

The TraceGOLD TG-5SilMS with SafeGuard gives an outstanding peak shapes and separation for HAA and dalapon in water according to the EPA method 552.2.

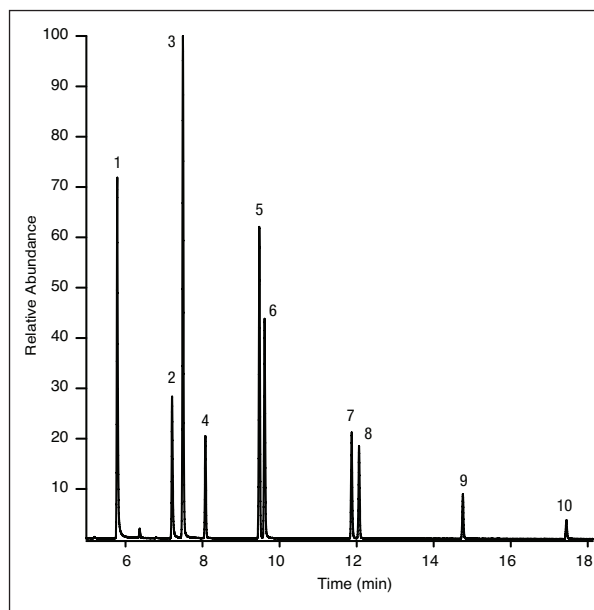


Figure 1. The chromatogram of  $m/z$  59 extracted from 50-300 amu full scan at 10 µg/mL of haloacetic acids and dalapon in water

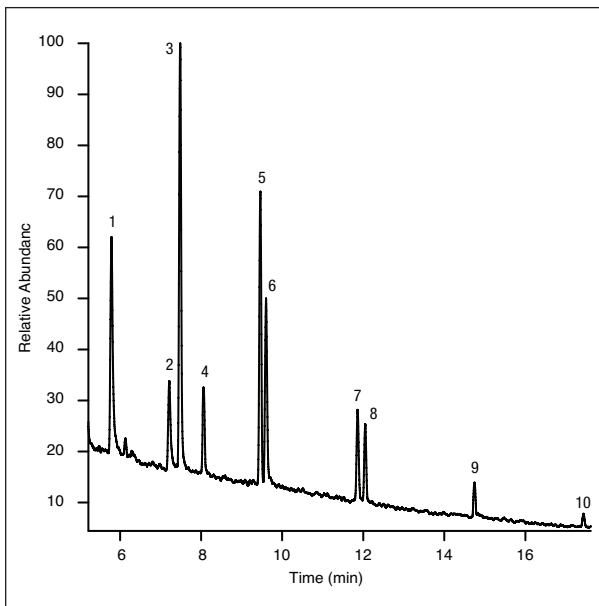


Figure 2. SIM of m/z 59 at 250 ng/mL of haloacetic acids and dalapon in water

Peak Number	Compound	Abbrev	Tr/min	%RSD (n=3)
1	Monochloroacetic acid	MCAA	5.79	14
2	Monobromoacetic acid	MBAA	7.21	18
3	Dichloroacetic acid	DCAA	7.48	15
4	Dalapon	-	8.06	13
5	Trichloroacetic acid	TCAA	9.46	10
6	Bromochloroacetic Acid	BCAA	9.60	14
7	Dibromoacetic acid	DBAA	11.86	12
8	Bromodichloroacetic acid	BDCAA	12.05	14
9	Chlorodibromoacetic acid	CDBAA	14.75	9
10	Tribromoacetic acid	TBAA	17.44	8

Table 1. Peak identification and extraction for haloacetic acids and dalapon at 250 ng/mL

## Conclusions

The TraceGOLD TG-5SilMS column with SafeGuard demonstrated excellent performance for the analysis of HAA and dalapon with minimum peak tailing of analytes. The excellent separation achieved by the TG-5SilMS with SafeGuard GC column would also be applicable to ECD detection as stated in the EPA method 552. The SafeGuard provides an added protection to the analytical column by extending the column lifetime.

## Reference

[1] EPA Method 552.2, Determination of haloacetic acids and dalapon in drinking water by liquid-liquid extraction, derivatization and gas chromatography with electron capture detection.

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