Application Note: ANCCSHACIDS

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

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**Key Words**

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

## Abstract

The performance and suitability of using an ultra low bleed sylarylene 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 quadrapole ISQ mass spectrometer.

The analytical column selected for this analysis was a Thermo Scientific ultra low bleed phase TraceGOLD TG-5SilMS 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-5SilMS 30m x 0.25 mm x 0.25 µm GC column with 10 m SafeGuard.

## Experimental Details

| Consumables | | Part Number |
|---|---|---|
| Column: | TraceGOLD TG-5SilMS 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 |
| Colum 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 |

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**Sample Preparation**

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|---|---|
| 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**

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|---|---|
| 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**

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|---|---|
| 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 |

## 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 dalpon 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.

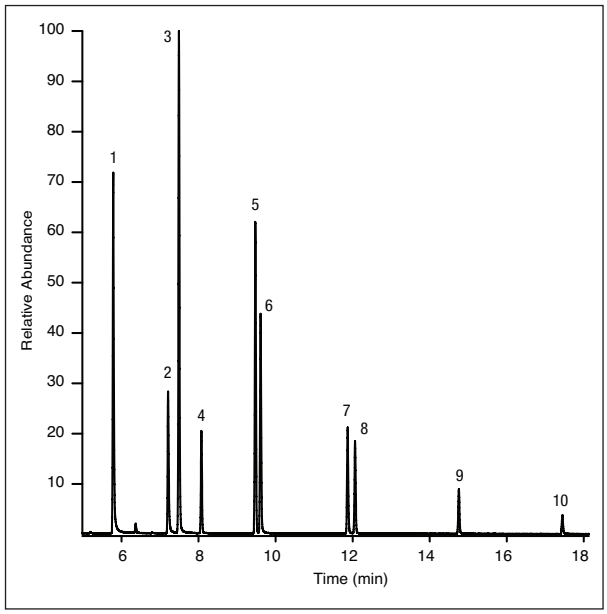


Figure 1. The chromatogram of m/z 59 extracted from 50-300 amu full scan at 10 µg/mL of haloacetic acids and dalapon in water

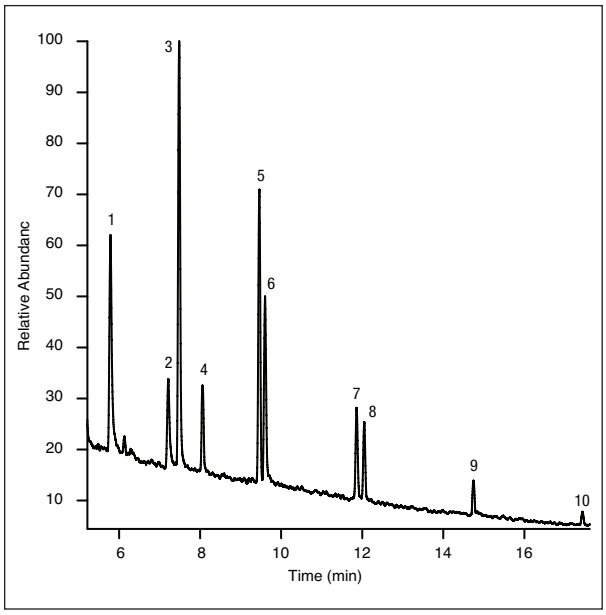


Figure 2. SIM of m/z 59 at 250 ng/mL of haloacetic acids and dalapon in water

| Peak Number | Compound | Abbrev | Tr/min | %RSD (n=3) |
|---|---|---|---|---|
| 1 | Monochloroacetic acid | MCAA | 5.79 | 14 |
| 2 | Monobromoacetic acid | MBAA | 7.21 | 18 |
| 3 | Dichloroacetc 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 acheived 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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