

EPA Method 522: Determination of Selected Organic Contaminants by Agilent Model 240 GC/MS/MS

Application Note

Authors

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Abstract

Low level detection of 1,4-dioxane is required. The detection limits vary with regulatory requirements from state to state and country to country. As instrument sensitivity has improved, it has become possible to detect compounds at lower and lower levels. This application note investigates the detection of 1,4-dioxane down to a 0.02 ug/L level using an Agilent 240 Ion Trap in the EI/MS/MS mode.

Introduction

The US EPA has classified 1,4-dioxane as a probable human carcinogen. This compound is associated with a number of other health concerns ranging from skin, lung, and eye irritation, to headaches and anorexia. There are several exposure pathways, namely inhalation of vapors, ingestion of contaminated food and water, or dermal contact. 1,4-Dioxane has also been classified as an emerging contaminant.

Because of its widespread use as a chlorinated solvent stabilizer, 1,4-dioxane may be found in the presence of high concentrations of 1,1,1-trichloroethane.

In 2008, the EPA developed EPA Method 522 for the analysis of 1,4-dioxane in water to improve detection limits, precision, and accuracy. It describes a solid phase extraction of sample, followed by extract concentration to 1 mL, and injection into a GC/MS in selected ion monitoring (SIM) mode.

This application note shows the use of MS/MS easily meets the demands of EPA Method 522.



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Experimental

Calibration standard solutions

A series of calibration standards to encompass the desired calibration range were prepared. The calibration standards contained varying amounts of 1,4-dioxane, with fixed amounts of both the Surrogate and the Internal Standard, prepared in DCM. The number of standards required was determined by the calibration range. Three standards were required for one order of magnitude, six standards for two orders of magnitude and nine standards for three orders of magnitude.

The calibration curve associated with this application note data contained nine standards with concentrations of 1,4-dioxane ranging from 0.001 µg/mL to 0.50 µg/mL. (This corresponds to a concentration range of 0.02–10 µg/L in the drinking water samples.) The lowest standard is ½ the level of the lowest concentration required by EPA Method 522.

The concentrations of both 1,4-dioxane-d8 (SUR) and THF-d8 (IS) were 0.200 µg/mL in each standard.

Calibration

Calibration curve

The GC/MS MassHunter Software was used to create a calibration curve for 1,4-dioxane using the Internal Standard calculation technique. Concentrations were determined through the use of a linear calibration curve. Because the surrogate is added to all samples and standards at a single concentration, the calibration for the surrogate was accomplished using the average response factor.

Calibration acceptance criteria

When quantitated using the calibration curve, each calibration point, except the lowest point, should quantitate within 80–120% of its true value. The lowest point should quantitate within 60–140% of its true value.

Experimental conditions

All analyses were performed on an Agilent 7890A GC System equipped with an Agilent 7693 Automatic Sampler and an Agilent 240 Ion Trap GC/MS in Electron Ionization (EI) mode. MS/MS was used to enhance selectivity and sensitivity.

Ion trap setup parameters for 522

Ion Trap temperature	200 °C
Manifold temperature	60 °C
Transferline temperature	250 °C
Autotune	
Scan type	EI/MS/MS

GC setup parameters for 522

Column	20 m × 150 µm, 0.84 µm VF-624
Flow column	0.5 mL/minute
Oven	35 °C hold for 1.0 minutes 7 °C/min to 90 °C no hold, 50 °C/min to 280 °C
Equilibrium/stabilization time	2 minutes

MS/MS setup

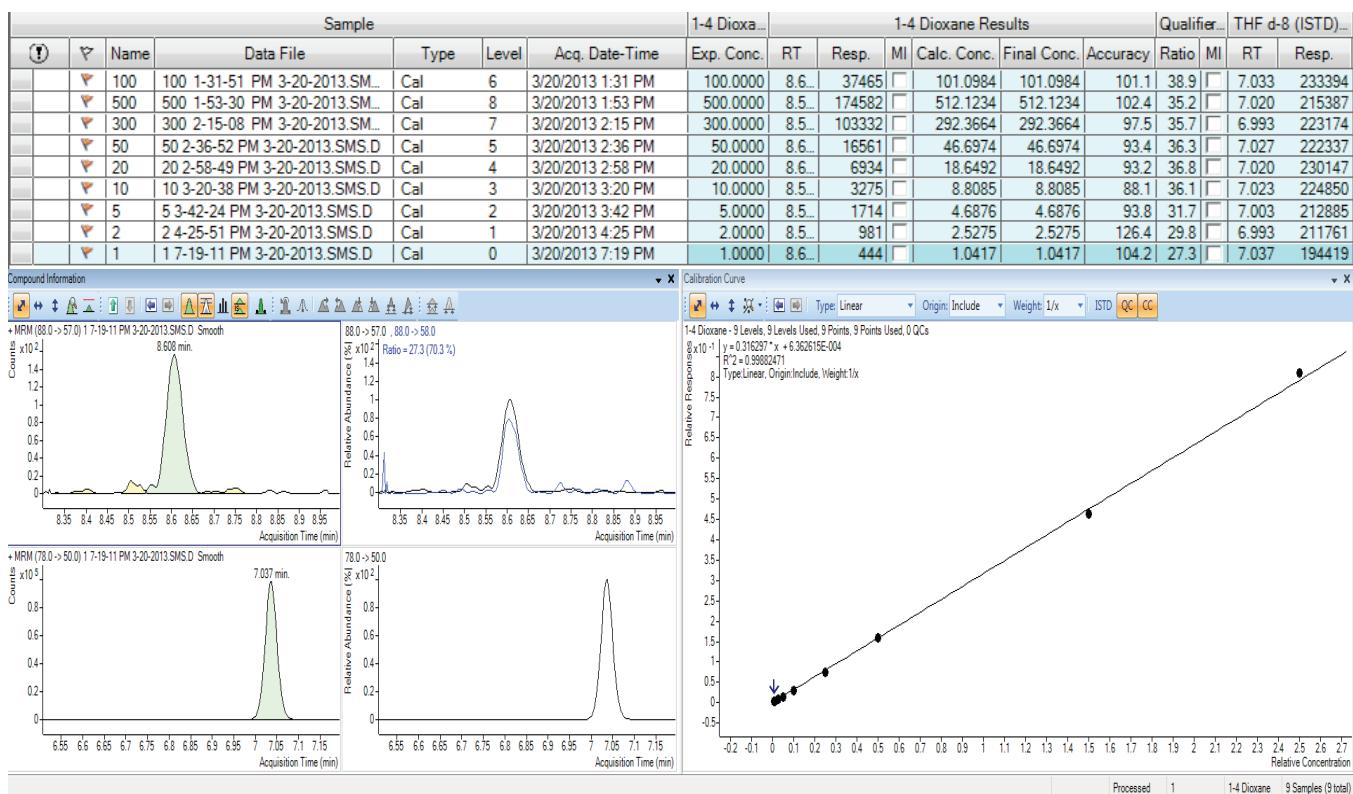
Compound	Precursor ion	Isolation window	Waveform	Excitation storage	Excitation amplitude	Product ion start	Product ion end
THF-d8(IS)	78	1	Resonant	29.7	0.2	40	78
1-4 dioxane	88	1	Resonant	33.5	0.21	50	88
1-4 dioxane d8	96	1	Resonant	36.6	0.21	50	96

GC setup parameters for 522

- MMI Injector operated in the pulsed splitless mode
- Insert - 2 mm dimple liner (p/n 5190-2297)
- 200 °C isothermal
- Purge flow to split vent 60 mL/min at 0.5 minutes
- 2 µL injection volume

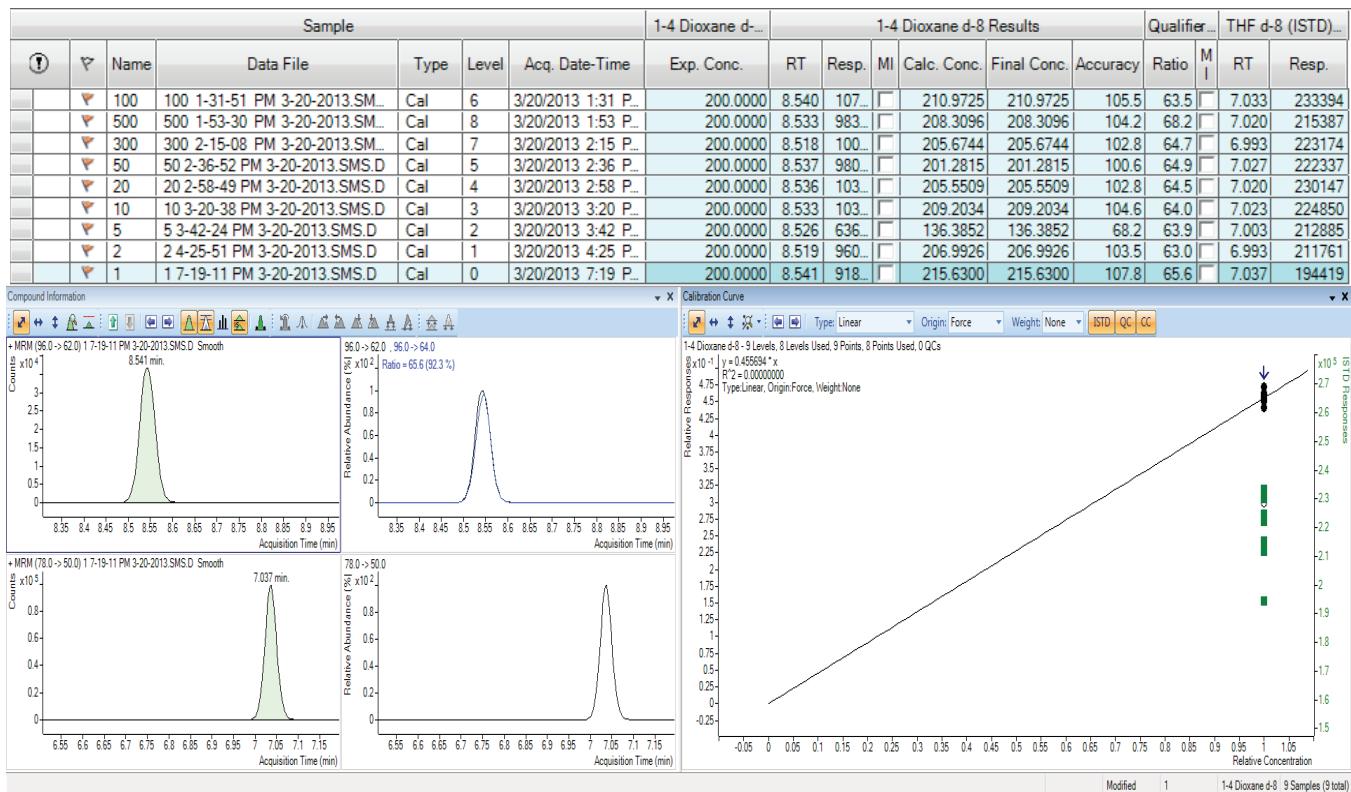
Results and Discussion

Calibration from 1–500 ng/mL
1-4 dioxane, shown is the 1.0 ng/mL level



Surrogate 1-4 dioxane d-8

Green squares are IS THF d-8 response



Eight replicates at 1.0 ng/mL to determine the method detection limit (MDL), limit of quantitation (LOQ), and limit of detection (LOD) values

- MDL - 0.2353 ng/mL
- LOQ - 0.7849 ng/mL
- LOD - 0.2355 ng/mL
- Signal-to-noise (S/N) - 120.88
- Calculations were automatically done from the MassHunter Software

Calculate MDL-LOQ-LOD Outlier Limit

Name	TS	RT	Transition	Avg Conc.	Std. Dev.	Avg Conc./Std.	Conc. RSD	MDL	LOQ	LOD	Noise	S/N	Avg Height	Avg. Resp	Resp. RSD
1-4 Dioxane	4	8.597	88.0->57.0	1.1367	0.0785	14.48	6.9	0.2353	0.7849	0.2355	1.74	120.88	186	442	4.6
1-4 Dioxane d-8	4	8.479	96.0->62.0	220.8871	4.6674	47.33	2.1	13.9927	46.6743	14.0023	6.56	6328.71	38723	93618	2.9

Conclusion

This application note presents a sensitive, selective, and robust method to determine 1,4-dioxane in samples using THF d-8 as an internal standard. For the analysis of 1,4-dioxane, the benefits of Agilent GC Quadrupole Ion Trap MS/MS capability cannot be underestimated.

In terms of reducing sample matrix interference, improving S/N, and coupling its high selectivity and sensitivity, the GC Quadrupole Ion Trap MS/MS provides a more confidence driven solution for the analysis of 1,4-dioxane.

GC Quadrupole Ion Trap MS/MS analysis has the potential to reduce false positive and negatives as well as providing an additional degree of confidence in the results obtained.

Using the optimized method listed above, a fast, targeted GC/MS/MS method can be used to solve the current analysis problem facing laboratories today.

References

- EPA Methods 522, 624, 625, 8015B, 8260B, 8270C.
- Emerging Contaminant – 1,4-dioxane. September, 2009. EPA 505-F-09-006.
- EPA Administrator Jackson Outlines New Vision for Clean, Safe Drinking Water. USEPA Press Release: 3/22/2010.
- EPA Method 522: Determination of 1,4-dioxane in drinking water by solid phase extraction (SPE) and gas chromatography/mass spectrometry (GC/MS) with selected ion monitoring (SIM). Version 1.0, September 2008.

For More Information

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