

The Analysis of 2,3,7,8-TCDD in Drinking Water Using an Approved Modification of EPA Method 1613B by Tandem Gas Chromatography Mass Spectrometry

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Introduction

Recently, the Environmental Protection Agency (EPA), Office of Ground Water's Technical Support Center, has determined that gas chromatography coupled with tandem mass spectrometry (GC/MS/MS) can be used in place of high resolution gas chromatography mass spectrometry (HRGC/MS) for the analysis of dioxins using EPA Method 1613B(1). EPA considered this modification as "minor", and data for compliance monitoring under the National Primary Drinking Water Regulations (NPDWR) can be accepted as long as a) the laboratory demonstrates it can meet the quality control requirements listed in the method and b) any positive results are confirmed qualitatively by HRGC/MS. This position by EPA clearly allows for a much more cost-effective approach to dioxin analysis since bench top triple quadrupole mass spectrometers are a fraction of the cost of high resolution instruments. A method for the analysis of 2,3,7,8-TCDD in drinking water is described here.

Materials and Method

The mass spectrometer system used to generate the data consisted of a Varian Model 1200 Triple Quadrupole coupled to a Varian Model 3800 gas chromatograph equipped with a temperature programmable injector, Model 1079, and a Varian Model 8400 autosampler. The analytical column was a CP-Sil8 CB, 60 meters x 0.25 mm ID x 0.25 micron film thickness.

Sample preparation procedures were taken directly from EPA 1613B, in which 1 L of sample was extracted using a 47 mm solid phase extraction (SPE) disk available from a variety of vendors. The disk was eluted with small quantities of toluene and evaporated with nitrogen to approximately 100 ul. The extract was cleaned up with small amounts of silica gel, then evaporated further to a final volume of 10 ul. 10 ul of the internal standard was added to the extract just prior to analysis.

The extract was injected into the gas chromatograph under the following conditions:

GC Column oven program: Initial temperature 130 C, hold for 3 min. 130 C to 200 C at 3 C/min., hold 0.5 min.; 200-230 at 2.4 C/min., hold 18.5 min.; 230 C to 290 C at 20 C/min., hold 3.5 min. The gas chromatograph was equipped with electronic flow control, allowing for a 45 psi pressure pulse to be applied during the splitless phase of the injection. The split vent was allowed to be open for 0.2 min. prior to splitless injection in order to vent excess solvent. Between 2 and 5 ul are typically injected. The initial injector temperature was 125 C and ramped 200 C/min. up to a final temperature of 300 C. The mass spectrometer was set up in multiple reaction mode (MRM) to isolate and monitor the masses listed below.

Table 1: Transitions Monitored in Data Acquisition

Masses isolated in Q1	Masses isolated and detected Q2
321.9 (Target 2,3,7,8-TCDD)	257
	259
327.9 (Recovery Standard)	263
333.9 (Labeled 2,3,7,8-TCDD)	268
	270

The ions used for quantitation were the Q2 ions listed above. The filament and electron multiplier were set to obtain

maximum sensitivity. As a check for mass accuracy, the spectrometer was tuned with FC-43 calibration gas according to the manufacturers instructions.

Results and Discussion

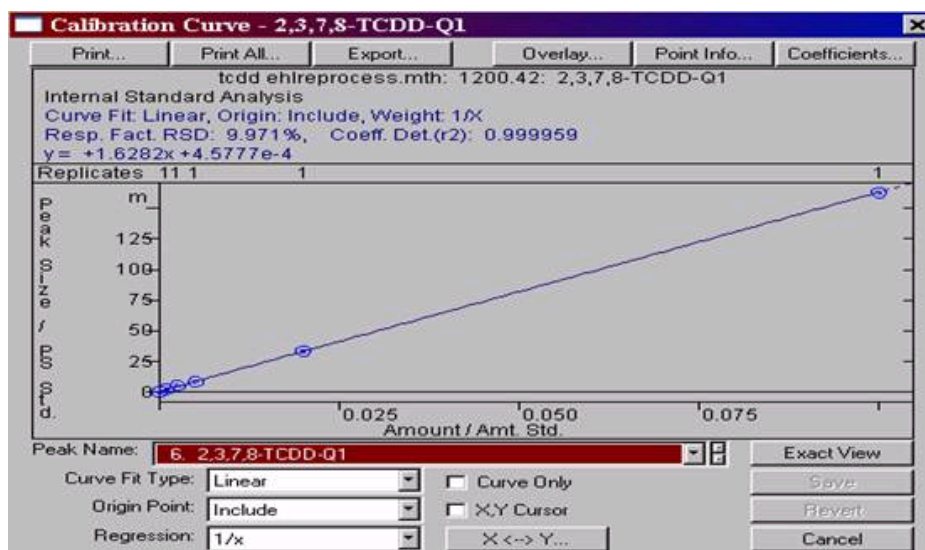
The analytical method described here was developed for drinking water systems that must comply with the NPDWR regarding the level of 2,3,7,8-TCDD in public water supplies. The maximum contamination level in drinking water is currently listed as 30 pg/L (2). Many state regulatory agencies, however, require that dioxin in drinking water be reported down to levels between 2 and 5 pg/L. Although EPA Method 1613B is the only currently approved method for this analysis, data generated by the original method authors did not robustly meet the more stringent reporting requirements by some state agencies. In fact, the calculated method detection limit (MDL) in 1613B for 2,3,7,8-TCDD is 4.4 pg/L. Method detection limits are based upon statistical results obtained from a series of replicate reagent water spikes taken through the entire analytical process. This calculated limit does not represent a quantitation limit, and is therefore typically inappropriate to use as a reporting limit.

Method validation for the modified method was performed in three parts: a) Demonstration of calibration linearity, b) Precision and accuracy by the performance of a Demonstration of Capability (DOC), and c) Method Detection Limit (MDL) studies. In addition, several untreated ground and surface drinking water sources were spiked at low levels (5 to 10 pg/L). Any positive results in field samples were confirmed by HRGC/MS in order to gain confidence in the specificity of the procedure.

Calibration

The following illustration is typical of the types of calibration curves achieved during the development of the method. Calibration range is from 0.1 ng/ml (2 pg/L) up to 200 ng/ml (2000 pg/L). RSDs routinely obtained were less than 10 % with correlation coefficients of 0.999 or greater.

Figure 1: Calibration Curve for 2,3,7,8-TCDD



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Method detection limit and Demonstration of Capability were performed using the protocol described in EPA 1613B. DOC data was generated by analyzing 4 replicate reagent water samples spiked at 200 pg/L. Average percent recoveries ranged from 95%-108% on two separate studies with RSDs < 1%. MDL replicates were analyzed at a concentration of 5 pg/L resulting in calculated MDLs between 1 and 2 pg/L.

Figures 2 and 3 below illustrate excellent sensitivity at levels between 2 and 10 pg/L. The sum of product ions 257 and 259 are used for quantitation. Each ion is also quantitated separately and used to obtain isotopic ratios for

comparison to expected abundances. This provides additional qualitative information to definitively identify 2,3,7,8-TCDD.

Figure 2: Low-level spikes in reagent water at 2 pg/L

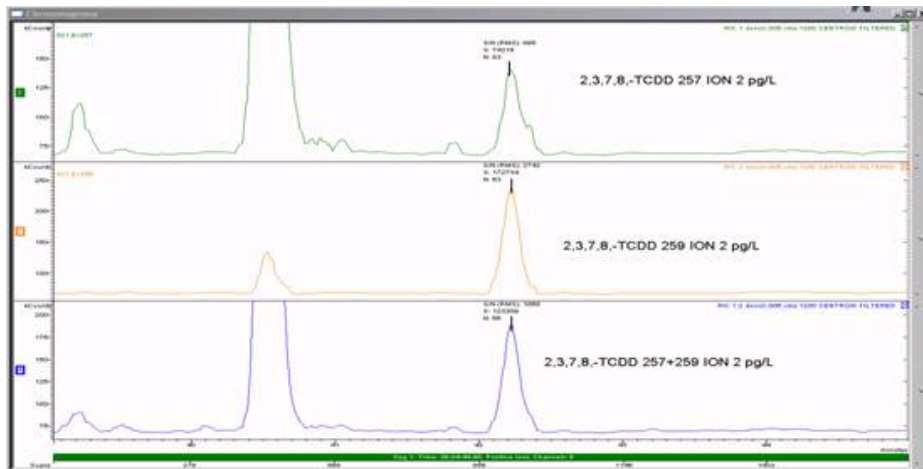
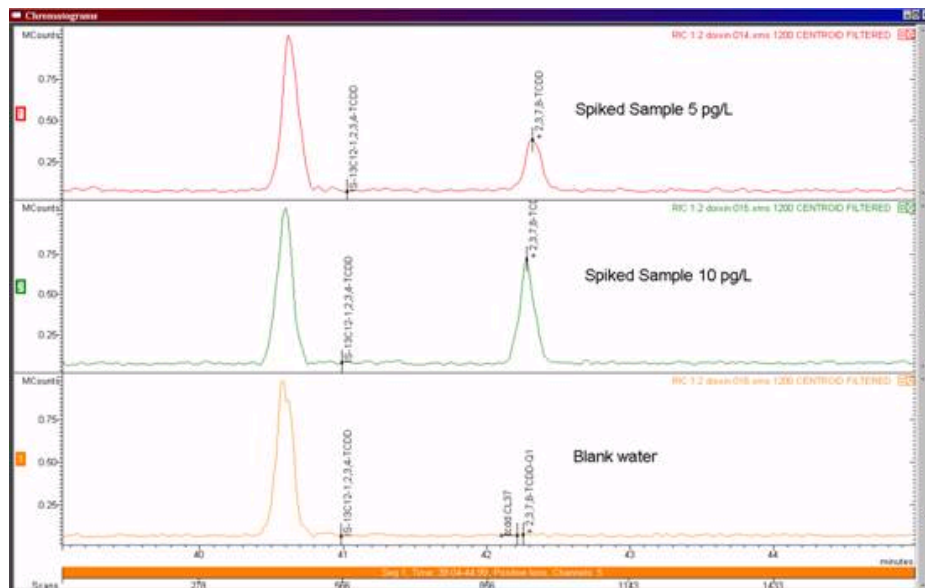


Figure 3: Low-Level spikes in ground water samples



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References

USEPA Office of Water, Engineering and Analysis Division, Method 1613: Tetra- Through OctaChlorinated Dioxins and Furans by Isotope Dilution

HRGC/HRMS, October 1994.

- National Primary Drinking Water Regulations listed maximum contamination levels (MCLs) in drinking water, available at the USEPA website <http://www.epa.gov/safewater/mcl.html>.