



# SEMI-VOLATILE ORGANICS IN DRINKING WATER using EPA Method 525.2 optimized for greater sensitivity

Elaine A. LeMoine

## Introduction

The US EPA Drinking Water Manual contains the methods used to identify and quantify regulated and unregulated organic drinking water contaminants. Included in this manual is Method 525.2, a Gas Chromatographic/Mass Spectrophotometric (GC/MS) technique for the determination of semi-volatile organic compounds. Method 525.2 can be used for the identification and quantification of a group of analytes known as Acid Extractables and Base Neutrals. The number of compounds that can be determined using this technique is extensive and includes a large number of regulated and unregulated drinking water contaminants.

Drinking water regulations specify acceptable levels below which it has been determined human health will not be adversely affected. In many cases these regulatory levels require extremely sensitive analytical techniques.

This extensive analyte list, and the extreme sensitivity requirements, make EPA Method 525.2 one of the most challenging.

US EPA methods incorporate stringent quality control (QC) and quality assurance (QA) criteria. It is imperative that the technique used for the identification and quantification of compounds, which can endanger human health, meet the quality objectives. Compliance with these criteria ensures compliant data that can be used with confidence.

The TurboMass™ Mass Spectrometer and AutoSystem™ XL Gas Chromatograph provide results compliant with the drinking water objectives. Table I lists recommended chromatographic conditions for performing this method. Table II lists the mass spectrophotometric conditions.

## Tuning

Many factors will affect the performance of a GC/MS system. Initially,

the MS must be optimized to meet standard performance criteria. The Perkin-Elmer TurboMass MS automatically optimizes the mass spectrometer parameters for compliance with the EPA Tune criteria. DFTPP is analyzed to verify system performance and must be repeated once for every 12 hours of analysis time. Tuning is only required when the analysis of DFTPP shows noncompliance with the EPA abundance ratio criteria. Figure 1 displays

Table I. Chromatographic Conditions

Perkin-Elmer AutoSystem XL	
Column	PE-5MS 30 m x 0.25 mm; 0.25 µm film thickness
Oven Temperature Program	40°C for 1 min, 45°C/min to 160°C for 3 min; 6°C/min to 320°C for 2 min
Programmable Pneumatic Control (PPC)	Helium at 1.0 mL/min
Injector	250°C
Injection Volume	1 µL

Table II. Mass Spectrometer Conditions

Perkin-Elmer TurboMass	
Mass Scan Range	45–450 m/z
Scan Speed	2.0 scans/sec
Filament Delay	3.0 min
Ion Source Temperature	150°C
Transfer Line Temperature	250°C
Ionization Mode	EI

the chromatogram, spectrum, and library match results for DFTPP at 5 ng. The spectrum shows an excellent match to the National Institute of Standards and Technology (NIST) mass spectral library and meets the EPA ion abundance criteria.

### Calibration

The initial calibration requires six standards containing each analyte of interest and a constant concentration of each internal standard and surrogate. The suggested concentrations listed in Method 525.2 are 0.1, 0.5, 1.0, 2.0, 5.0, and 10.0 ng/ $\mu$ L. There are exceptions, based on the sensitivity and expected

concentration of specific analytes. Response factors for each analyte are calculated using the internal standard technique and the following calculation:

$$RF = (A_{(x)}C_{(is)}) / (A_{(is)}C_{(x)})$$

where:

$A_{(x)}$  = Area of the characteristic ion for the compound being measured

$A_{(is)}$  = Area of the characteristic ion for the specific internal standard

$C_{(is)}$  = Concentration of the specific internal standard

$C_{(x)}$  = Concentration of the compound being measured

These *Relative Response Factors* (RRFs) are used to calculate the average RRF for every compound. The percent relative standard deviation (%RSD) is calculated using the average RRFs from the initial calibration. The calibration curve is considered compliant when the %RSD of the average RRF for each analyte is less than 30%. All the analytes in Table III were analyzed at concentrations of 0.10, 0.50, 1.00, 2.00, 5.00, and 10.00 ng. All internal standards and surrogates were analyzed at the mid-level range of 5 ng. Every compound complied with

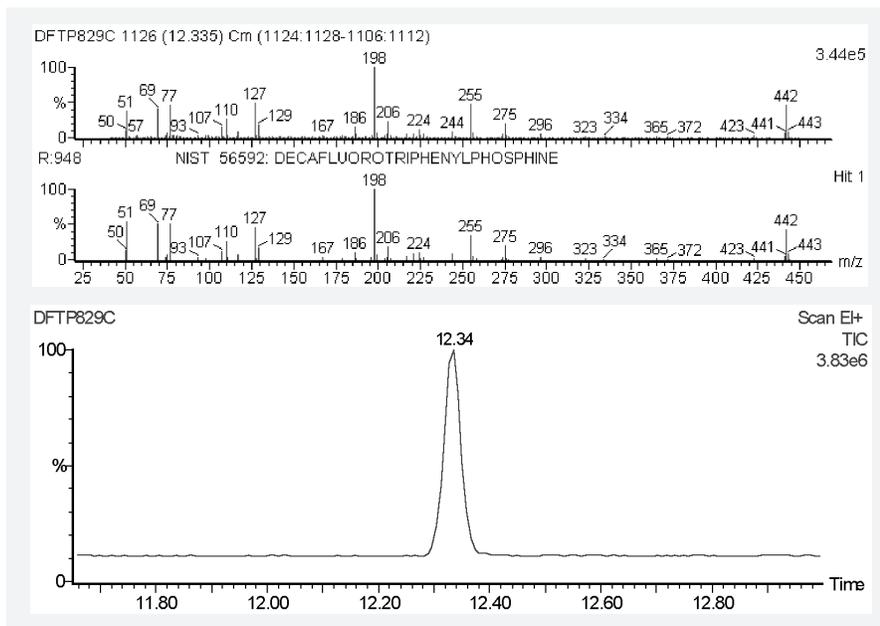


Figure 1. Chromatogram and spectrum of 5 ng of DFTPP.

Table III. Initial Calibration Results for EPA Method 525.2

Method 525.2 Initial Calibration Results					
Compound	RRF%	RSD	Compound	RRF%	RSD
2,2,4,4-Tetrachlorobiphenyl	0.37	11.4	Dimethyl phthalate	1.25	13.3
2,3-Dichlorobiphenyl	0.60	13.2	Dimethylnitrobenzene	0.33	2.1
2,4,5-Trichlorobiphenyl	0.64	16.9	Fluorene	1.13	12.8
2-Chlorobiphenyl	0.83	16.9	Heptachlorobiphenyl	0.05	21.3
Acenaphthylene	1.98	12.4	Hexachlorobenzene	0.32	16.2
Anthracene	2.10	8.5	Hexachlorobiphenyl	0.19	12.1
Benz(a)anthracene	0.50	16.7	Indeno(1,2,3-cd)pyrene	0.37	20.8
Benzo(a)pyrene	0.49	15.1	Isophorone	1.13	10.1
Benzo(b)fluoranthene	0.52	18.8	Pentachlorobiphenyl	0.24	12.1
Benzo(ghi)perylene	0.44	20.2	Perylene-d12	0.48	3.9
Benzo(k)fluoranthene	0.44	18.0	Phenanthrene	2.29	9.6
bis(2-ethylhexyl) phthalate	1.13	9.8	Pyrene	1.92	10.1
Chrysene	0.53	14.7	Pyrene-d10	1.65	4.0
Dibenz(a,h)anthracene	0.38	20.2	Triphenylphosphate	0.13	9.8
Diethyl phthalate	1.62	22.2			

the %RSD criteria demonstrating calibration linearity. An example of this is illustrated in Figure 2.

## High sensitivity method

### Tuning

Many compounds analyzed using this methodology have extreme sensitivity requirements. The TurboMass MS tune parameters can be optimized to achieve even greater sensitivity. Relaxing the mass resolution slightly while maintaining DFTPP performance can increase signal intensity. Figure 3 displays the results from the analysis of 5 ng of DFTPP relative to the acceptance criteria in Method 525.2. The chromatographic response of this peak, compared to that seen in the previous example, is greater and the results are still compliant.

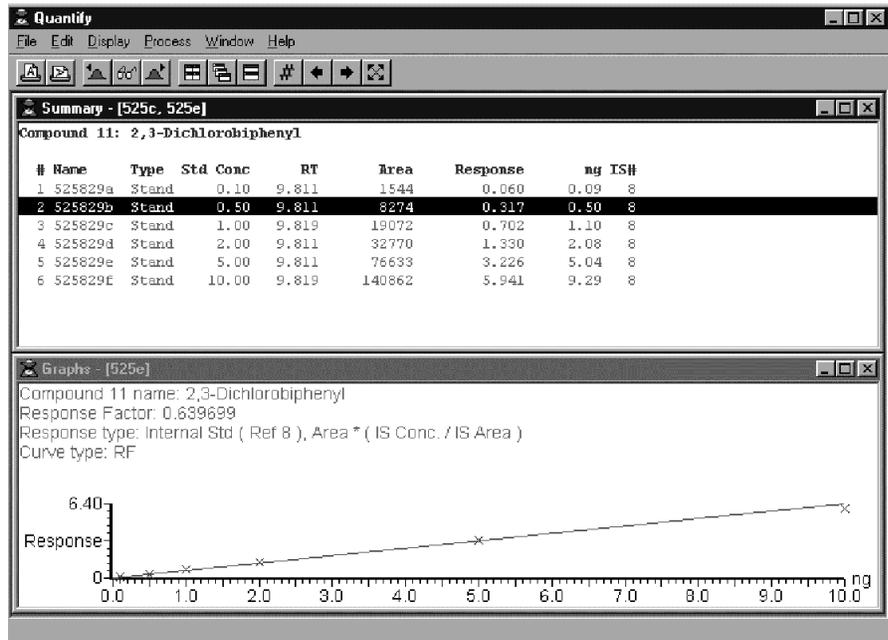


Figure 2. Results and Calibration Curve for 2,3-Dichlorobiphenyl.

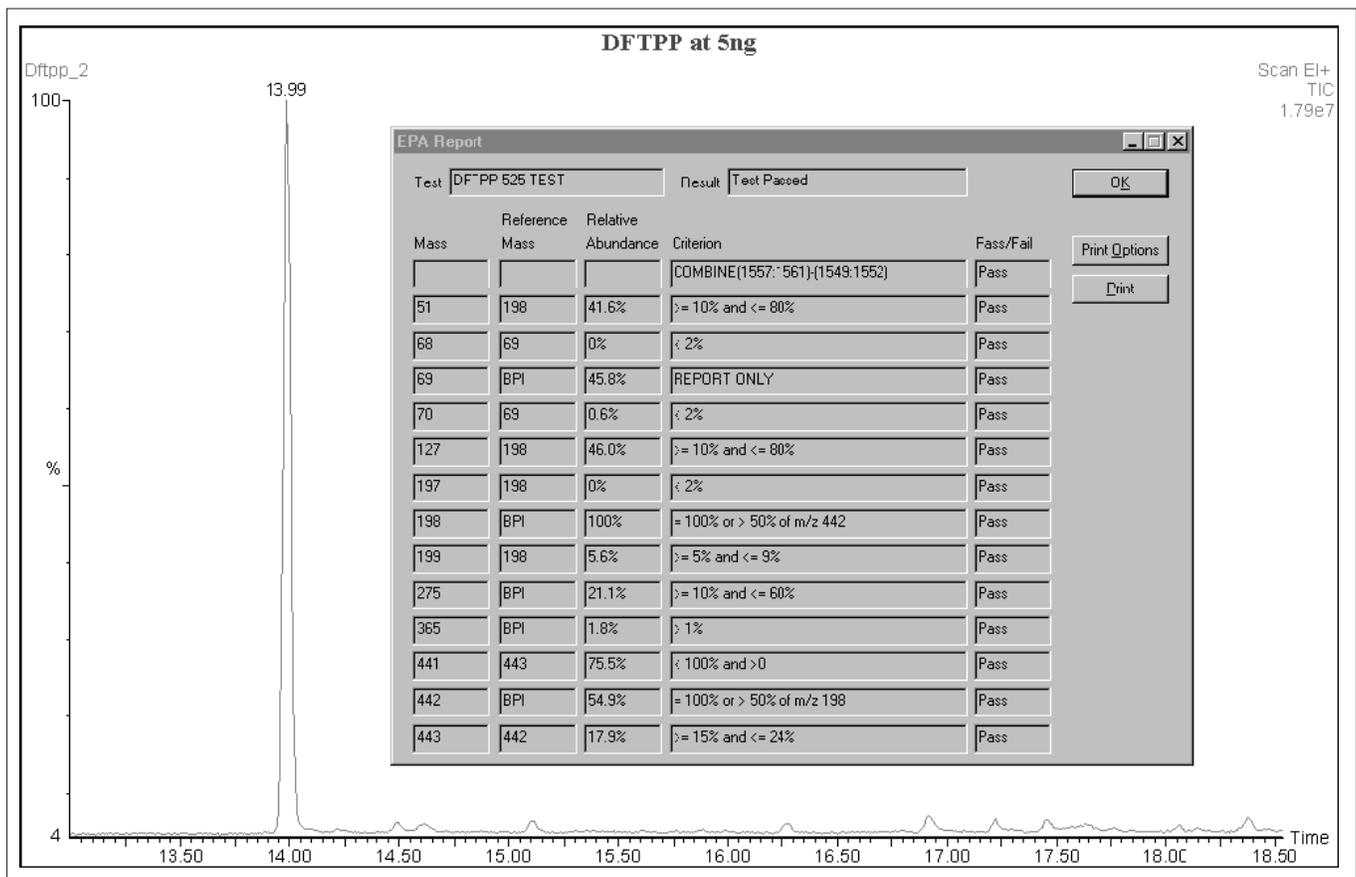


Figure 3. Chromatographic Peak of 5ng of DFTPP and Tune Results.

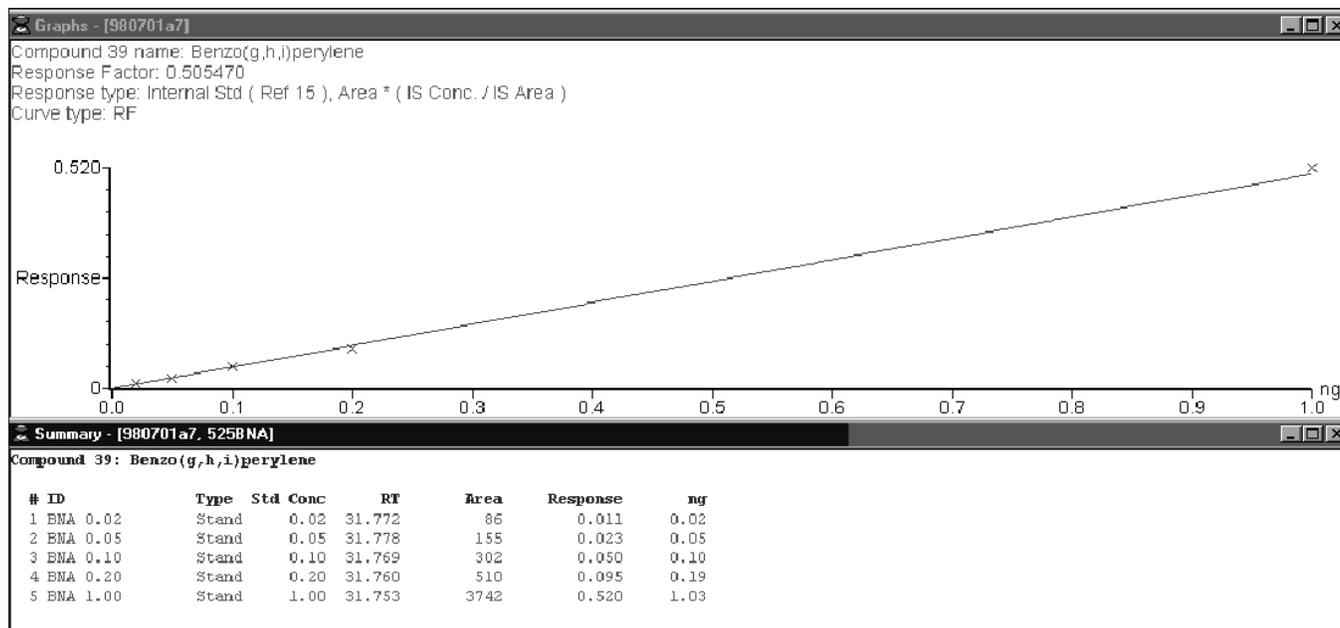
### Calibration

The calibration range was adjusted to focus the analysis on the more critical low-level measurements. Five standards were analyzed at concentrations of 0.02, 0.05, 0.10, 0.20, and 1.00ng. Internal Standards and Surrogates were included at concentrations of 0.05ng each per standard. The Method 525.2 criteria were used to evaluate the initial calibration. Every analyte met the 30% RSD criteria and is listed in Table IV. The results and calibration curve for benzo(g,h,i)perylene are displayed in Figure 4.

**Table IV. Initial calibration results for low level method 525.2**

Initial Low Level Calibration Results					
Compound*	%RSD	Compound	%RSD	Compound	%RSD
Isopherone	24.7	Anthracene	16.5	Chrysene	7.2
1,3-Dimethyl-2-nitrobenzene	11.9	Trichlorobiphenyl	18.8	bis(2-ethylhexyl)phthalate	30.0
Dimethyl phthalate	14.7	Tetrachlorobiphenyl	13.1	Benzo(b)fluoranthene	12.6
Acenaphthylene	4.0	Pentachlorobiphenyl	19.0	Benzo(k)fluoranthene	6.6
2-Chlorobiphenyl	5.7	Pyrene	15.6	Benzo(a)pyrene	15.4
Diethyl phthalate	28.8	Hexachlorobiphenyl	18.3	Perylene-d12	10.5
Fluorene	24.3	Triphenylphosphate	26.1	Indeno(1,2,3-cd)pyrene	11.1
2,3-Dichlorobiphenyl	17.6	Heptachlorobipheyl	17.4	Dibenz(a,h)anthracene	27.4
Hexachlorobenzene	6.9	Benz(a)anthracene	6.9	Benzo(g,h,i)perylene	7.1
Phenanthrene	17.1				

\*Pentachlorophenol was omitted due to known sensitivity problems.



**Figure 4.** Results and Calibration Curve for Low-Level Standard Benzo(g,h,i)perylene.

## Detection Limits

Detection limit determination is described in the General Method Features of "Methods for the Determination of Organic Compounds in Drinking Water"<sup>(1)</sup>. It states, "Most methods include either a method detection limit (MDL) or an estimated detection limit (EDL) for each analyte. ...The EDL is either the MDL, or a concentration of compound in a clean water matrix that gives a peak in the final extract with a signal-to-noise ratio of about 5." Figure 5 shows the selected ion chromatogram for Acenaphthylene at 0.02 ng, and its internal standard Acenaphthene-d10 at 0.05 ng. The calculated signal-to-noise ratio for Acenaphthylene is 82, substantially above noise level and the EDL minimum of 5. The spectrum and library search match are shown in Figure 6 and serve to illustrate the spectral quality attainable even at these low levels. Method detection limits will vary depending on the extraction technique, the sample size, the sample matrix, and the project requirements. The regulated components have varying levels of sensitivity requirements. For example, in the US, di-(2-ethyl-hexyl)phthalate is limited to a concentration of 6 µg/L in drinking water whereas benzo(a)pyrene has a maximum contaminant level of 0.2 µg/L. Clearly, benzo(a)pyrene has far greater sensitivity requirements that can be addressed using a more sensitive technique.

## Conclusions

EPA method 525.2 is one of the most challenging. Using the TurboMass Mass Spectrometer and the AutoSystem XL, the analytical

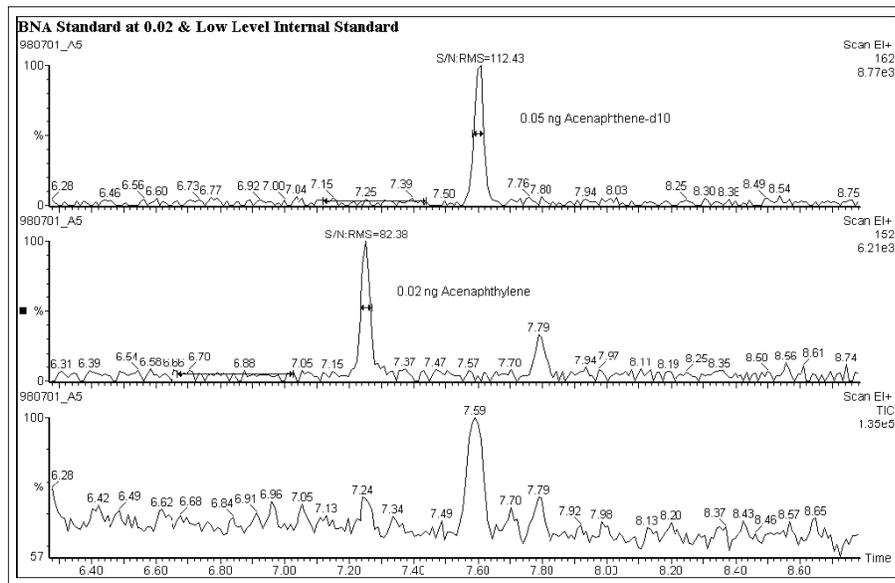


Figure 5. Calculated Signal-to-Noise for Acenaphthylene and Acenaphthene-d10.

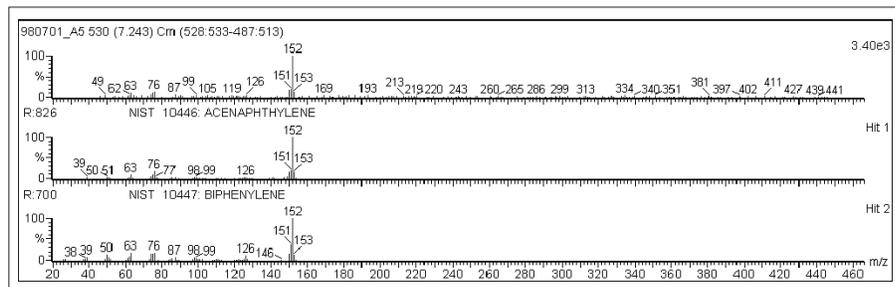


Figure 6. Library Search Results for 0.02ng of Acenaphthylene.

range can be optimized for even greater sensitivity gains. By relaxing the mass resolution, peak signal can be increased since "...overall sensitivity increases as resolution is reduced."<sup>(2)</sup> Clearly, the sensitivity gains realized by optimizing the TurboMass MS for low-level determinations provide the extra margin of confidence needed when reporting critical drinking water contaminants that can impact human health.

## References

- (1) Methods for the Determination of Organic Compounds in Drinking Water Supplement III, National Exposure Research and Development U.S. EPA, Cincinnati, OH.
- (2) Message, Gordon M.; Practical Aspects of Gas Chromatography/Mass Spectrometry, 1984.

**PERKIN ELMER**

*Look to us. And see more.*

Visit our Website at [www.perkin-elmer.com](http://www.perkin-elmer.com).

**The Perkin-Elmer Corporation**, 761 Main Avenue, Norwalk, CT 06859-0010 USA

Tel: (800) 762-4000 or (203) 762-4000 • Fax: (203) 762-4228



Perkin-Elmer is a registered trademark and TurboMass and Autosystem are trademarks of The Perkin-Elmer Corporation.

Order No. D-5886

September 1998

KG0998005

Printed in USA. © 1998 The Perkin-Elmer Corporation