Generation of AQA Standards for EPA Method 8270 Using the Agilent 7696A Sample Prep WorkBench

Application Note

Environmental

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Abstract

Using the Agilent 7696A Sample Prep WorkBench to prepare calibration standards enables relative response factor reproducibility and recoveries that are well within the analytical quality assurance standards set by this laboratory for EPA Method 8270.

Introduction

Analytical quality assurance (AQA) is essential for the proper operation of any analytical laboratory, be it commercial, government, or academic. Reliability of data, particularly for analyses regulated by the Environmental Protection Agency (EPA), depends on strict adherence to a wide range of operating procedures for analysis. Two of the most common procedures are the use of calibration curves and the measurement of recovery from spiked samples.

A calibration curve is constructed by preparing a series of standards across a range of concentrations near the expected concentration of analyte in the unknown sample. The deviation of individual calibration points from the line of best fit is used to assess the precision of the calibration. This precision is directly dependent on the quality of the source standard material used as well as the accuracy and reproducibility of the preparation of the calibration standards. Measurement of recovery of analyte from a sample spiked with a standard is another assessment of the efficiency and precision of the analysis, and is also dependent on the quality of the calibration standards used.

Calibration standards are most commonly prepared manually, involving tedious and time-consuming pipetting steps whose accuracy is dependent on the skill of the operator and the possibility of human error. In addition, the operator may be exposed to hazardous chemicals. Automated dispensing systems remove human error from the process, and assure the accuracy and precision of the preparation of the calibration standards.

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This application note demonstrates the ability of the Agilent 7696A Sample Prep WorkBench to automatically prepare calibration standards that meet AQA requirements for calibration curve precision and recovery levels. EPA Method 8270 for the detection of semi-volatile organic compounds (SVOCs) was used as a model for the demonstration. This method uses gas chromatography/mass spectrometry (GC/MS) to analyze solid, liquid, and gaseous samples for a list of 90 SVOCs regulated by the EPA.

The automated method for preparing the calibration standards resulted in standards that met the laboratory's AQA requirements for relative standard deviation of the calibration curve average relative response factors (RRFs) for 13 calibration check compounds (CCCs). Recoveries were also within allowed limits for these 13 compounds. Additionally, all other requirements outlined by the method for system performance compounds (SPCCs) and non-CCC compounds were met.

Experimental

Standards and Reagents

Methylene chloride of pesticide grade or higher was used to prepare the calibration standards. SVOC standards were obtained from Sigma-Aldrich and Restek, at a concentration of 1,000 µg/mL. Deuterated internal and surrogate standards were also obtained from Restek.

Instruments

The calibration standards were prepared on an Agilent 7696A Sample Prep WorkBench using the settings shown in Table 1. The analysis was performed by GC/MS.

Table 1.   Agilent 7696A Sample Prep WorkBench Settings

Front syringe	500 µL
Back syringe	100 µL
Heater setpoint	Ambient
Heater offset	0 °C
Number of pumps	2
Wash volume	400 µL
Draw speed	800 (µL/min)
Dispense speed	2,500 (µL/min)
Draw needle depth offset	0 mm
Viscosity delay	4 seconds
Overfill	5% of syringe size
Air gap	0% of syringe size
Sample processing scheme	Sequential

Preparation of Calibration Standards on the Sample Prep WorkBench

Calibration standards were prepared sequentially on the WorkBench. Varying amounts of methylene chloride were first dispensed into vials, then varying amounts of the SVOC standard working solution were dispensed into the same vials to provide a total volume of 1 mL in each vial, and eight calibration standards ranging in concentration from 0.5 to 80 µg/mL. The syringe was rinsed with 400 µL of methylene chloride between each dispensing step.

Results

Calibration Curves

The GC/MS analysis of SVOC calibration standards results in separate peaks whose area can be integrated to relate peak area to concentration (Figure 1). Response factors are calculated at each concentration on the calibration curve by dividing the area of the peak by the concentration of the calibration standard. An RRF is then calculated by dividing the response factor of the calibration standard by the response factor of the internal standard.
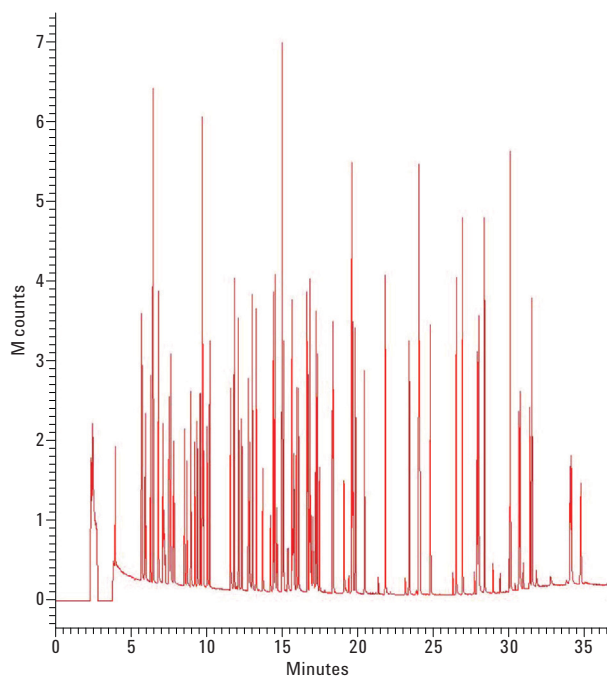

Figure1.   Typical total ion current (TIC) chromatogram obtained for an EPA Method 8270 GC/MS analysis, spiked at 10 µg/mL with calibration standard mix.

An average RRF is calculated across all concentrations of the calibration standard used to generate the calibration curve. Each average RRF is determined in replicate and the relative standard deviation (RSD) is calculated across the replicates. The AQA standard in this laboratory requires that the RSDs be calculated for 13 CCCs, and that they must be less than 30%. Table 2 illustrates that all of the RRFs for the CCCs generated using the WorkBench met this quality criterion. In fact, 8 of the 13 RSDs were ≤10%.

Recoveries

Recoveries of spiked calibration standards were determined using the calibration curves prepared using the WorkBench. The AQA standard in this laboratory requires that all recoveries fall in the range of 80 to 120%. Table 3 shows that all recoveries met this criterion, and 7 of the 13 measured recovery values were in the 95 to 100% range. These high recoveries attest to the accuracy of quantitation using the calibration curves derived from standards prepared by the WorkBench automated system.

Table 3.　Recoveries for Spiked Calibration Standards

Calibration check compound	% Recovery
Phenol	114.21
1,4-Dichlorobenzene	97.28
2-Nitrophenol	99.69
1,2,4-Dichlorophenol	108.1
Hexachlorobutadiene	98.53
4-Chloro-3-methylphenol	96.33
2,4,6-Trichlorophenol	95.71
Acenapthylene	92.92
N-Nitrosodiphenylamine	97.70
Pentachlorophenol	115.06
Fluoranthene	89.91
Di-*n*-octyl phthalate	108.55
Benzo[a]pyrene	99.05

Table 2.　Relative Response Factors (RRFs) Across the Calibration Curve, Average RRFs, and % RSDs

Calibration check compound	RRF for each concentration (µg/mL) on the calibration curve								Average RRF	%RSD
	0.5	1.0	2.0	5.0	10	20	50	80		
Phenol	1.581	1.502	1.597	1.722	1.413	1.342	1.053	1.082	1.412	17.1
1,4-Dichlorobenzene	1.600	1.618	1.848	1.725	1.710	2.074	1.722	2.030	1.791	10.0
2-Nitrophenol	0.119	0.113	0.106	0.114	0.116	0.111	0.126	0.109	0.114	5.3
2,4-Dichlorophenol	0.330	0.306	0.332	0.330	0.338	0.293	0.299	0.280	0.314	6.8
Hexachlorobutadiene	0.227	0.230	0.241	0.265	0.283	0.261	0.283	0.312	0.263	11.2
4-Chloro-3-methylphenol	0.417	0.416	0.420	0.422	0.442	0.379	0.438	0.464	0.425	5.8
2,4,6-Trichlorophenol	0.529	0.495	0.476	0.460	0.477	0.451	0.410	0.403	0.463	9.1
Acenapthylene	2.195	2.137	1.960	2.012	2.062	1.914	1.962	2.389	2.079	7.6
N-Nitrosodiphenylamine	0.868	0.795	0.721	0.673	0.650	0.646	0.658	0.678	0.711	11.3
Pentachlorophenol	0.157	0.140	0.129	0.136	0.128	0.118	0.094	0.088	0.124	18.8
Fluoranthene	1.006	0.961	0.948	0.920	0.956	0.990	0.972	1.147	0.988	7.1
Di-*n*-octyl phthalate	2.038	2.557	2.825	3.159	3.281	3.471	4.018	--	3.050	21.2
Benzo[a]pyrene	1.092	1.080	1.069	0.984	0.951	0.914	0.987	1.060	1.017	6.6

Conclusion

Preparation of accurate and precise calibration standards is an absolute necessity for every analytical laboratory. This is particularly true for EPA methods in environmental laboratories. Method 8270 is challenging due to the large number of chemically diverse compounds analyzed. The Agilent Sample Prep WorkBench provides the precision and accuracy required for an analytical laboratory to obtain reportable EPA Method 8270 results, without the tedium, time, and human error associated with manual preparation of calibration standards.

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