Your local **gas generation** partner

Performance of Method 8270 Using **Hydrogen** Carrier Gas

Performance of Method 8270 Using **Hydrogen** Carrier Gas

Introduction

USEPA Method 8270 [1] for semivolatiles is used by laboratories to measure a mixture of acids, bases, and neutrals in a wide variety of matrices. Sample extracts can range from clean water to sludge coming from Superfund clean-up sites. The complexity of these extracts demand a robust instrument that is easy to operate and maintain. Adding to method complexity is the uncertainty in both cost and supply of helium, forcing some laboratories to consider hydrogen as carrier gas. Hydrogen is not an inert gas; it is reactive and can be an explosion hazard if allowed to build up in either the GC oven or manifold of a mass spectrometer.

The Scion Helium-free Package will ensure safe routine operation, with little or no performance change for EPA Method 8270. Scion's unique axial ion source design provides excellent robust operation and minimizes unwanted protonation and spectral distortions. In addition, the Gas Chromatograph with Scion Split/ Splitless (SSL) injector and inert pathway prevent compound degradation and reactions with hydrogen.

Gas Chromatograph and Mass Spectrometer Conditions

Gas Chromatograph and Mass Spectrometer Conditions	
Gas Chromatograph	Scion 436
Inlet	Scion SSL (Split/Splitless)
Mode	Pulsed Split Injection, 0.5 µL
Injection Temp	290°C
Pressure Pulse	40 psi for 0.3 min
Split Flow	70 mL/min
Gas Type	Hydrogen
Gas Supply	Peak Precision 500 Trace H_2 Generator
Inlet Liner	SGE 4 mm ID Liner w/ goose-neck, p/n 092017

Oven

Oven Ramp	°C/min	Temp °C	Hold (min)
Initial		45	3.0
Ramp 1	25	100	1.0
Ramp 2	10	310	1.0
Total Run Time	28 min		

Column

SGE BP-5MS, 20 m x 0.18 mm x 0.18µm, p/n 054301
Constant Flow 1.0 mL/min Hydrogen Carrier

Mass Spectrometer	SCION Select SQ with Helium-free Package
Solvent Delay	2 minutes
Scan Range	45-500 da
Dwell Time	250 ms
Ion Source Temp	330°C
Transfer Line Temp	300°C

Experimental

The recommended instrument and operating parameters are listed in Table 1. When using hydrogen carrier for the first time, more hydrocarbon background is observed but will clean up over time. This initial background can be reduced significantly by increasing the ion source temperature to 350 °C, with hydrogen column flow at 4 mL/min and filament turned ON for 4 hours.

Calibration standards were obtained from Restek Corporation, Bellefonte PA, MegaMix p/n 31850, containing 76 target compounds. The calibration for most analytes ranged from 1 to 200 ppm. Internal and surrogate standards were added at a concentration of 40 ppm. Solvent: Dichloromethane.

A pulsed split injection was used to minimize contact and residence time of compounds inside the inlet. This is critical in hydrogen carrier gas, due to its low viscosity and tendency to react with dichloromethane and form HCl. Figure 1 illustrates the pulsed split injection technique with the Scion SSL.

The single goose-neck 4 mm open inlet liner is commonly used with Method 8270. It does not contain glass wool. Glass wool could contribute to compound degradation, especially when using reactive hydrogen as carrier gas.

Pulsed Split Injection

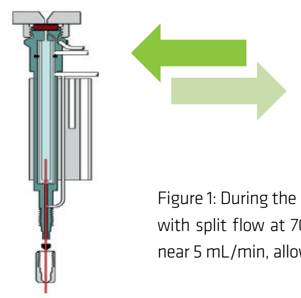


Figure 1: During the pulsed split injection, the inlet is set to 40 psi with split flow at 70:1. Under this condition, the column flow is near 5 mL/min, allowing rapid transport of analytes to column.

Results

In order for hydrogen carrier gas to be considered for use, Method 8270 specifications in terms of tuning, resolution, calibration, peak shape (Gaussian Factor), and system performance checks (SPCCs) must be met. In addition, the solvent specified in the method is dichloromethane (DCM), therefore essential to minimize degradation in the inlet. The GC/MS system must also produce mass spectra that match NIST library and demonstrate robust operation in heavy matrices.

The SCION with Helium-free Package can be auto-tuned normally and used with the tune-to-target feature for passing DFTPP tune. Figure 2 illustrates a DFTPP spectrum and report generated with the EnivroPro™ software.

The viscosity of hydrogen changes at a much slower rate vs. temperature than helium, and is an advantage for maintaining good solubility in the stationary phase during the GC oven ramp. Also, at a flow of 1.0 mL/min using the 20 meter 0.18 mm ID column, an optimal linear velocity for peak separation is maintained. This assures that the peak resolution criteria in the method is met, as illustrated in Figure 3 for Benzo(b) and Benzo(k) fluoranthene. The peak Gaussian Factor or peak Tailing Factor for Pentachlorphenol demonstrates the inert behavior of the system.

Tune with Hydrogen Carrier Gas

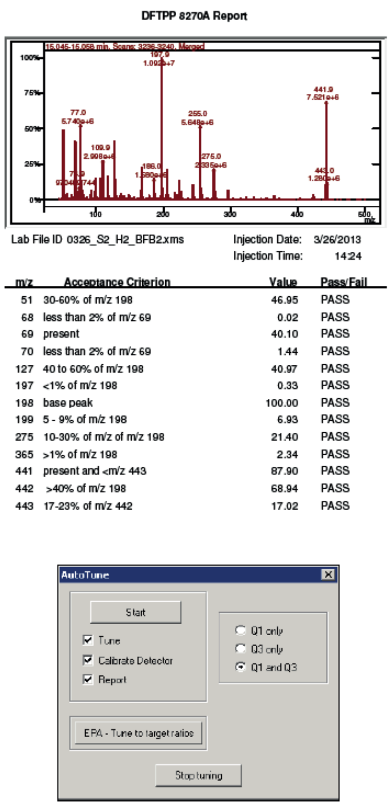


Figure 2: Auto-tune and tune-to-target work without modification using hydrogen carrier. DFTPP report easily generated from EnviroPro™ Software Package.

EnviroPro™ Software Reports

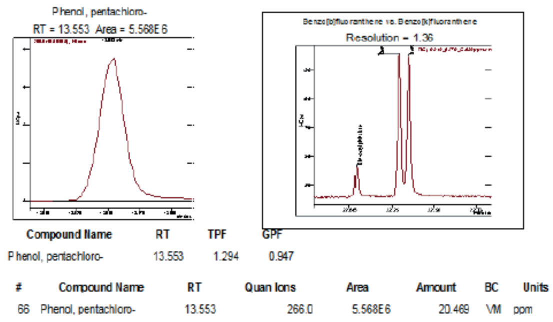


Figure 3: SPCC Peak Gaussian report for Pentachlorophenol (left) and Peak Resolution Test for Benzo(b) and (k) Fluoranthene generated using EnviroPro™ Software.

The SPCCs and initial calibration criteria are also met with hydrogen carrier. For the SPCCs the relative response factors (RRFs) are measured and compared to the criteria given in Table 2.

Compound	Method 8270 Min. RRF	RRF ON SCION Select SQ
N-nitroso-di-n-propylamine	0.05	0.715
Hexachlorocyclopentadiene	0.05	0.178
2,4-Dinitrophenol	0.05	0.070
4-Nitrophenol	0.05	0.134

An example calibration curve of Hexachlorocyclopentadiene is shown in Figure 4, with % RSD and corr. coefficient (r2) for this compound of 3.9% and 0.9998, respectively.

Calibration with Hydrogen Carrier Gas

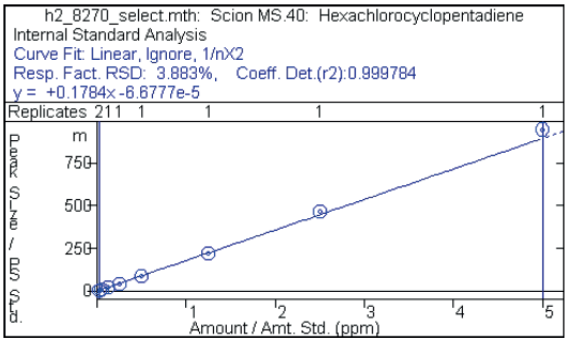


Figure 4: Calibration curve for Hexachlorocyclopentadiene with % RSD and corr. coefficient (r2) of 3.9% and 0.9998, respectively.

The overall average % RSD of all 76 compounds was 8.5%. Calibration for the critical quality control (QC) check and SPCC compounds are listed in Table 3, along with some %RSDs shown for very active compounds in Figure 5.

match hits at 900+ for 1,2,4-Trichlorobenzene and Dibutyl phthalate.

Quality control check compounds for Method 8270 pass using hydrogen as carrier gas

QC Check Compounds	Corr. Coeff.	Avg. RRF	%RSD	CCC	SPCC
Phenol	0.9980	0.722	11.9	PASS	
Benzen, 1,4-dichloro-	0.9985	0.980	7.6	PASS	
1-Propanamine, N-nitroso-N-propyl-	0.9981	0.719	8.5		PASS
Phenol, 2-nitro-	0.9968	0.116	13.3	PASS	
Phenol,2,4-dichloro-	0.9981	0.114	8.4	PASS	
1,3-Butadi-ene,1,1,2,3,4,4-hex-acholor	0.9991	0.315	7.0	PASS	
Phenol, 4-cholor-3-methyl-	0.9958	0.147	9.8	PASS	
Hexachlorocyclo-pentadiene	0.9998	0.178	3.9		PASS
Phenol,2,4,6-trichloro-	0.9997	0.142	8.0	PASS	
Acenaphthene	0.9997	1.16	4.9	PASS	
Phenol,2,4-dinitro-	0.9993	0.070	14.5		PASS
Phenol,4-nitro-	0.9940	0.134	6.8		PASS
Phenol, pentachloro-	0.9994	0.082	14.2	PASS	
Fluoranthene	0.9998	1.42	6.3	PASS	
Di-n-octyl phthalate	0.9998	0.199	4.6	PASS	
Benzo[a]pyrene	0.9993	1.57	14.8	PASS	

The SPCC Compounds must have average RF>0.05 for initial calibration	PASS
The CCC compounds must have % RSD of RRFs for the initial calibration <30%	PASS
The overall average of all compound % RSDs must be <15%	PASS

Calibration Response Factors for Active Compounds

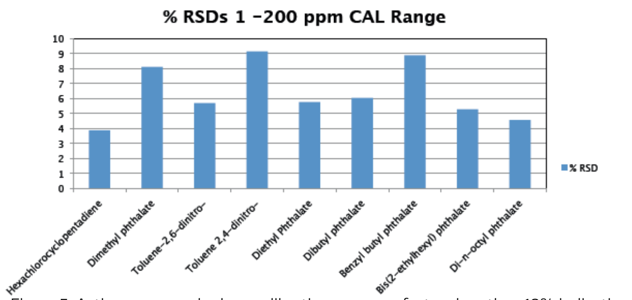


Figure 5: Active compounds show calibration response factors less than 10% indicating minimal reactivity with liner and ion source with hydrogen carrier and dichloromethane solvent.

Spectral quality may be problematic using hydrogen because unwanted protonation or other reactions in the ion source are possible. The Scion axial ion source design with Helium-free Package minimizes these reactions, as evidenced by good quality library matches to NIST. During this study, all 76 compounds were detected using automated AMDIS deconvolution/library search against NIST 11. Figure 6 illustrates example library

Excellent Library Matches with Hydrogen Carrier Gas

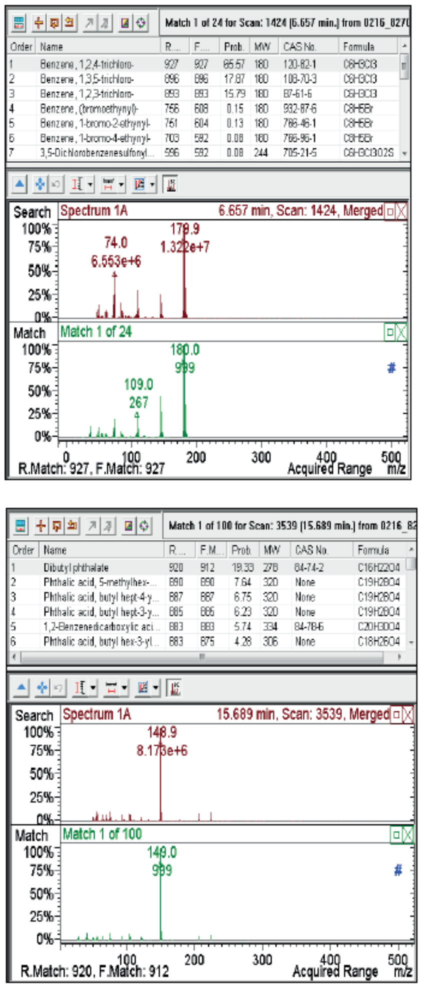


Figure 6: NIST library matches for 1,2,4-Trichlorobenzene and Dibutyl phthalate.

Method 8270 performance was tested using repeated injections of a contaminated sludge extract. A total of fifty injections were made, with an injection of the continuing calibration check (CCC) after every 10 extracts. The calculated concentration of the surrogates (target 40 ppm) and the % differences in response of the compounds were compared to the initial injection and then plotted. Figure 7 shows a TIC of the sludge extract. Figures 8 illustrates an example surrogate (2,4,6-Tribromophenol) and Figure 9 shows percent differences observed for the CCCs. As can be seen from the plots, excellent robust operation of the SCION Select SQ is maintained with hydrogen carrier.

Sludge Extract Injections

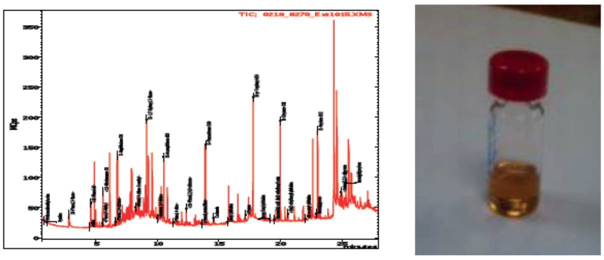
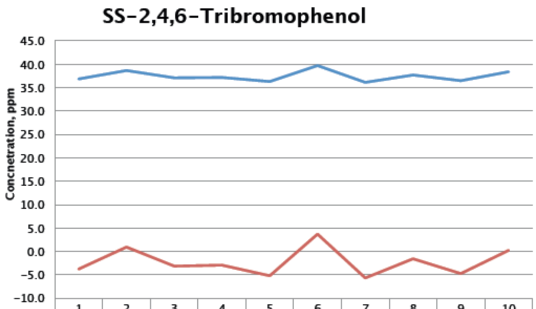


Figure 7: A Method 8270 sludge extract (right) was injected 50 times. A CCC was injected between every 10 extract injections for monitoring the % difference of surrogate and CCC compounds.

Surrogate Standard Recovery



	1	2	3	4	5	6	7	8	9	10
Observed Conc	36.9	38.7	37.1	37.2	36.3	39.7	36.1	37.7	36.5	38.4
% Difference	-3.8	0.9	-3.1	-2.9	-5.2	3.7	-5.7	-1.6	-4.7	0.2

Figure 8: The target concentration = 40 ppm, with % difference measured relative to initial CCC before extract injections.

Method 8270 performance was tested using repeated injections of a contaminated sludge extract. A total of fifty injections were made, with an injection of the continuing calibration check (CCC) after every 10 extracts. The calculated concentration of the surrogates (target 40 ppm) and the % differences in response of the compounds were compared to the initial injection and then plotted. Figure 7 shows a TIC of the sludge extract. Figures 8 illustrates an example surrogate (2,4,6-Tribromophenol) and Figure 9 shows percent differences observed for the CCCs. As can be seen from the plots, excellent robust operation of the SCION Select SQ is maintained with hydrogen carrier.

Continuing Calibration Check Stability

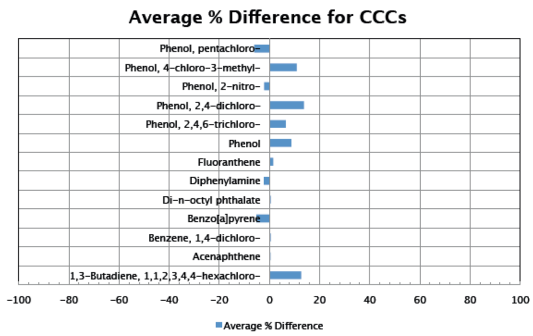


Figure 9: Target concentration = 20 ppm. The plot shows the average % difference for the base neutral and acid compounds in the CCC mixture over 50 matrix injections.

Conclusion

Method 8270 is a challenging method covering a wide variety of compound classes and matrix types. As the cost and scarcity of helium rises, laboratories have begun to convert methods to hydrogen carrier gas, due to the ability to safely produce it on demand with generators. Since hydrogen is a reactive gas and can develop explosive build-up in certain situations, a GC/MS solution must be safe and also produce data that pass both the qualitative and quantitative aspects of the method.

The Scion Select SQ has demonstrated excellent performance for Method 8270. The axial ion source, as well as the pulsed-split injection technique with the Scion SSL, was shown to produce excellent library-searchable mass spectra, passing quality control criteria, and robust operation in heavy matrices.

Author: Ed George

References

1. *USEPA Method 8270D, Revision 4, February 2017*

Acknowledgements

Peak Scientific for the use of the Precision 500 Trace Hydrogen Generator.

SCION INSTRUMENTS

PEAK SCIENTIFIC

*Your local **gas generation** partner*

www.peakscientific.com

Tel +44 141 812 8100 **Email** marketing@peakscientific.com