Application Note # CA 284780

Meeting Challenging Laboratory Requirements for USEPA Method 8270 Using a Highly Sensitive, Robust, and Easy-to-Use GC/MS

Abstract

The analysis of semi-volatile organic compounds (SOCs) using EPA Method 8270 presents challenges due to the wide variety of acids, bases, and neutrals that must be analysed in extremely complex sample extracts. Laboratories are under pressure from their customers to provide lower detection limits, faster sample turn-around-time, and detailed reports that contain all the validated quality control data. In addition, these labs want a GC/MS system that is easy to set up and manage, because constant requests for new target analytes increase the overall burden of data analysis and processing when changes to the existing method are required. The Scion Single Quadrupole (SQ) Mass Spectrometer is designed to meet these new challenges and provides a total solution to laboratories for USEPA Method 8270.

Introduction

Traditionally, USEPA Method 8270 has been used to analyze a variety of complex sample matrices using full scan GC/MS. Most labs analyze a subset of the compounds listed in the method, typically 75 to 100, at a calibration concentration range of 1 to 200 ppm. Newer versions of the method allow for the use of selected ion monitoring (SIM), which can significantly lower detection limits. Mixed mode scan methods, such as SIM/Scan, have the benefits of lowering detection limits and simultaneously providing full scan data for library search confirmation of target compounds and tentative identification of any unknown peaks in a chromatogram.

To take full advantage of this mixed mode approach the mass spectrometer must be capable of fast acquisition speed, especially if large numbers of compounds are added to the SIM component of the method. Secondly, the analytical system must have excellent sensitivity in the full scan mode, because library search results will be used for confirmation in many cases. Finally, the data acquisition and processing must be easy to maintain and manage in the mixed mode to meet the demand for the ever-increasing number of target compounds.

The Scion SQ meets these challenges by providing an inert ion source and revolutionary ion optics to obtain part-per-billion sensitivity in full scan analysis. In addition, software known as Compound Based Scanning (CBS) makes it easier than ever before to set up, optimize, and maintain complex mixed mode methods. Additional tools

such as tune-to-target and custom EPA reporting templates round out a complete solution for USEPA Method 8270.

Experimental

The following conditions were used for set up of the gas chromatograph and full scan mass spectrometry components of Method 8270. A pulsed-split injection was used for the analysis, which provided excellent sensitivity with a minimized amount of sample entering the column. The Scion SQ under these conditions is capable of easily detecting and quantitating concentrations of most analytes down to 75 ppb or lower in full scan, which is 10-100 times less than what is required in the method.

In the mixed scan mode, all 100 components were analyzed in full scan, along with 57 compounds in SIM mode. See Table 1 for analytes and SIM ions monitored for each.

Calibration standards were prepared at 0.075, 0.15, 1, 2, 5, 10, 30 ppm. Seventeen very dirty sludge extracts were provided by a local environmental laboratory, see Figure 1 showing an example extract.

451-GC Gas Chromatographic Conditions	
Column:	BR-5ms, 30 m x 0.25 mm x 0.25 um
Column Flow Rate:	1.0 mL/min constant flow
Injector:	Scion Split/Splitless injector, with 4 mm ID Siltek Fritted Liner (Part No.)
Injector Conditions:	40 psi pulsed split set 1:50 for 0.30 min at 250 °C
Column Temperature Program:	45 °C, hold 3 min, ramp to 120 at 30 °C/min, hold 1 min; ramp to 310 °C at 10 °C/min, hold 5 min.
Injection:	1.0 uL using Bruker 8400 auto sampler
Scion SQ Full Scan MS Conditions	
Scan Range:	45-450, unit mass resolution
Scan rate:	200 ms, positive ion polarity
Ion Source Temperature:	300 °C
Transferline Temperature:	280 °C
Filament Delay time:	2 min
Filament Emission Current:	80 uA

Compound Name	Retention Time	SIM Ion
N-Nitrosodimethylamine	3.639	74
2-Fluorophenol	5.177	112
Phenol-d5	6.106	99.1
Phenol	6.119	94.1
bis(2-chloroethyl)ether	6.212	93
2-Chlorophenol	6.290	128
1,4-Dichlorobenzene-d4	6.542	152
N-nitroso-di-n-propylamine	7.071	70
Nitrobenzene-d5	7.312	82
2,4-Dimethylphenol	7.892	107
2,4-Dichlorophenol	8.237	162
Naphthalene	8.524	128
4-Chloro-3-methylphenol	9.597	107
2-Methylnaphthalene	9.867	142.2
1-Methylnaphthalene	10.071	142.2
2,6-Dimethylnaphthalene	10.248	156
2,4,6-Trichlorophenol	10.491	196
2,4,5-Trichlorophenol	10.563	196
2-Fluorobiphenyl	10.673	172
2,3,4-Trichlorophenol	10.698	196
Biphenyl	10.885	154
Dimethylphthalate	11.633	163
Acenaphthylene	11.841	152.2
Acenapthene	12.242	153.2
2,3,5-Trimethylnaphthalene	13.139	170
Diethylphthalate	13.278	149.1
Fluorene	13.444	149.1

Compound Name	Retention Time	SIM Ion
Azobenzene	13.853	77
2,4,6-Tribromophenol	14.023	330
Hexachlobenzene	14.731	284
Pentachlorophenol	15.240	266
Phenanthrene-d10	15.658	188.1
Phenanthrene	15.714	178.2
Anthracene	15.834	178.2
Carbazole	16.281	167
1-Methylphenanthrene	17.188	192
Di-n-butylphthalate	17.195	149.1
Fluoroanthene	18.555	202.2
Pyrene	19.089	202.2
Terphenyl-d14	19.544	244.3
Butylbenzylphthalate	20.784	149.1
Chrysene	21.975	228.2
Benzo(a)anthacene	22.062	228.2
Bis(2-ethylhexyl)phthalate	22.176	149.1
Di-n-octylphthalate	23.649	149.1
Benzo(b)fluoranthene	24.376	252.2
Benzo(k)fluoranthene	24.436	252.2
Benzo(e)pyrene	24.945	252.2
Benzo(a)pyrene	25.047	252.2
Perylene-d12	25.171	264.2
Perylene	25.224	252.2
Indeno(123-cd)pyrene	27.469	276.3
Dibenz(ah)anthracene	27.531	278.3
Benzo(ghi)perylene	28.149	276.2

Table 1: SIM ions monitored in mixed mode on the Scion SQ

CBS is therefore a powerful tool to easily manage a large number of SIM ion acquisitions for a complex method like 8270. No need to worry about too many ions in a single segment, segment breaks, or whether one compound needs to be in more than one segment.

CBS also automatically creates the data handling method that is associated with the acquisition method, linking the tables. Therefore, if there is a change in the acquisition method, ie a compound added or deleted, the change will be reflected in the data handling method table as well. This saves the operator time because only one list of method compounds and conditions needs to be managed.

The mixed scan mode in CBS provides excellent sensitivity, as shown in the example chromatogram in Figure 8. Benzo(ghi)perylene is a PAH that elutes late in the chromatographic run, often with excessive column bleed. SIM monitoring provides clean baseline and enhanced signal-to-noise resulting in lower detection limits.

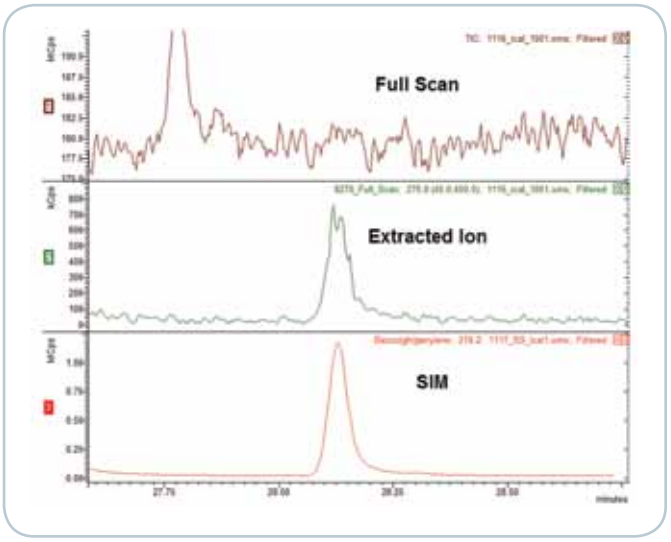

Figure 8: Mixed mode acquisition using CBS of 0.075 ppm calibration standard. Ion at m/z 276 can be extracted from the full scan data (green), but SIM run (red) simultaneously give best signal-to-noise and peak shapes to be used for low-level quantitation.

DFTPP can also be checked and will pass method criteria when the Scion SQ is operated in the mixed mode. This is because of the high speed scan rate combined with the optimal placement of the SIM scans in the acquisition. Another important aspect in the routine operation of the method is the ability to maintain good data quality while analysing dirty sample extracts. Since the Scion SQ is very sensitive, a pulsed-split injection can be used instead of a pulsed-splitless injection. Pulsed-split decreases the total amount placed onto the column, therefore increases the life of the column, liner, and thus improves throughput. Laboratories that analyse sludge extracts like that shown in Figure 1 often see loss of internal standards and poor peak shape after only a few injections. Continuing calibration checks (CCCs) are used to monitor the recovery of internal standards before and after sample extracts are run to ensure that there is minimal loss in sensitivity. An example of internal and surrogate standard peaks monitored in the CCC before and after 17 sludge extracts is shown in Table 3.

Standard	Perylene-d12	Phen-	Terphenyl-d14	Phenol-d5	Nitrobenzene-d5
Peak Area 1st CCC	93230000	2306000000	369600000	343800000	181700000
Peak Area Last CCC	71140000	2409000000	365400000	369000000	201100000
% Difference	23.69	4.47	1.14	7.33	10.68

Table 3: Peak areas in the CCC of internal and surrogate standards before and after sludge extracts. Peak shape and response were maintained in spite of over 30 injections of the sludge extracts, as shown in Figure 9 below.

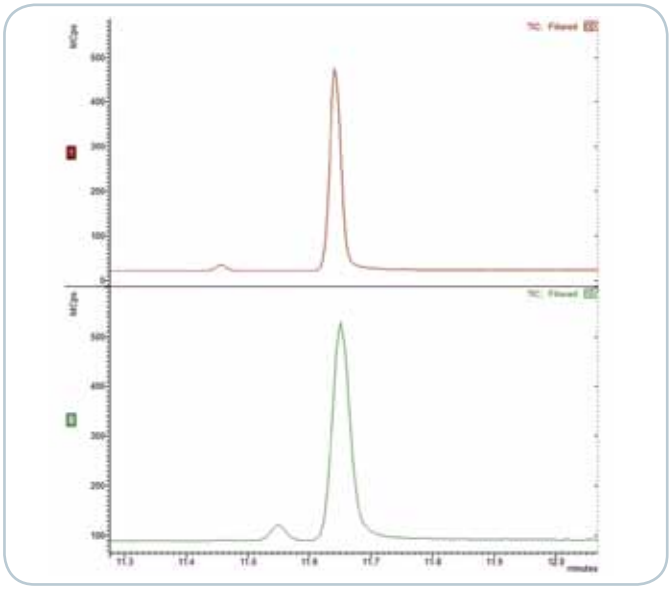

Figure 9: Excellent peak shape and response for pentachlorophenol is still maintained after 30 injections of sludge extracts. (Top- PCP peak before injection of extracts, Bottom-PCP peak after injection of extracts).

Reporting of the samples and quality control is the final step that must be completed by the lab. Scion offers EnviroPro™, a Microsoft Access database that will generate all of the required reports for EPA Method 8270, as well as several other methods. Example reports are tune criteria, method detection limit calculations, initial calibration reports, and continuing calibration checks. There are several graphic options available for printing chromatograms and target compounds, as well as unknown peaks (nontarget analytes). Qualitative interrogation of full scan data is another very important reason to run Method 8270 in the mixed mode.

Results

All users of USEPA Method 8270 know that passing the DFTPP tune is critical to the validity of the sample data. The Bruker Scion SQ has built-in tune-to-target ratio in mass calibration for DFTPP, as shown in Figure 2.

A tune report is easily generated using built-in report formats by simply selecting the data file and DFTPP peak, and then generating a pass/fail report as shown in Figure 3.

System Performance Check Compounds (SPCCs) are used to check the integrity of the liner/column and the inertness/cleanliness of the ion source region. Pentachlorophenol is a good test for active sites, as it tends to fail peak Gaussian test probes when the system becomes dirty. SPCCs can be injected and then immediately checked for degradation, Gaussian peak shape, or resolution in one easy reporting tool that is uses Microsoft Access to generate the required report. An example report for pentachlorophenol peak shape on the Scion SQ is shown in Figure 4.

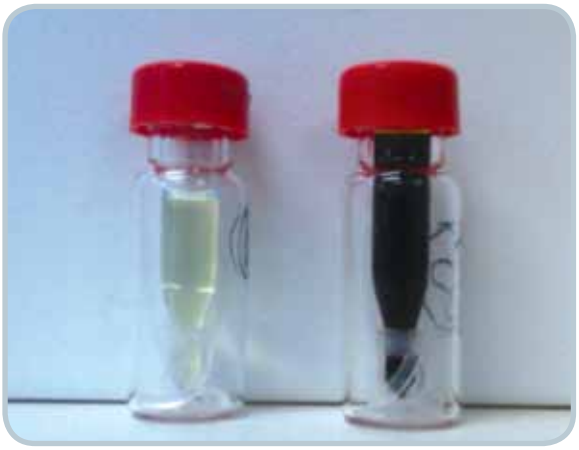

Figure 1: Clean extract (left), sludge extract (right)

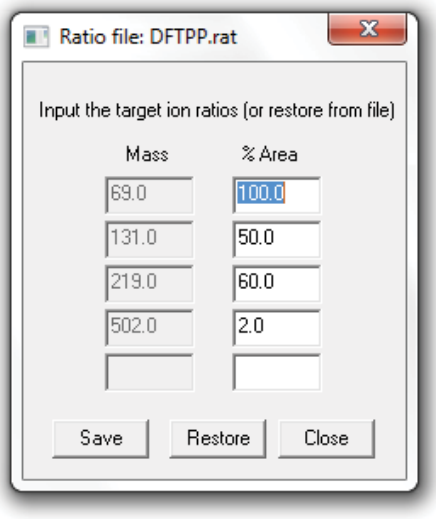

Figure 2: Tune-to-target for EPA tuning compounds are selectable in the software, and ratios can be easily edited if further optimization is required.

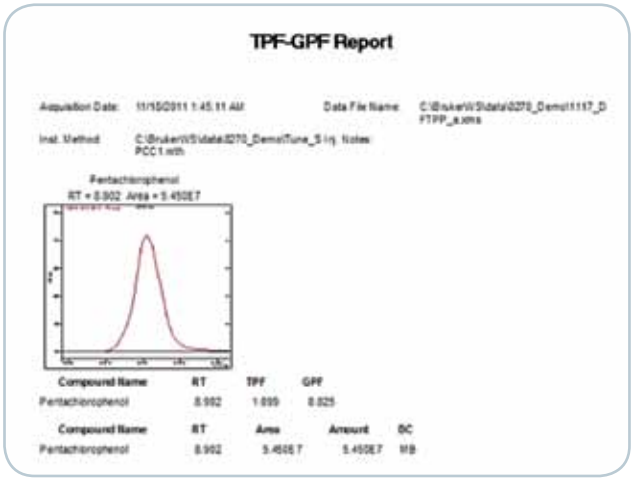

Figure 3: Example tune report for DFTPP

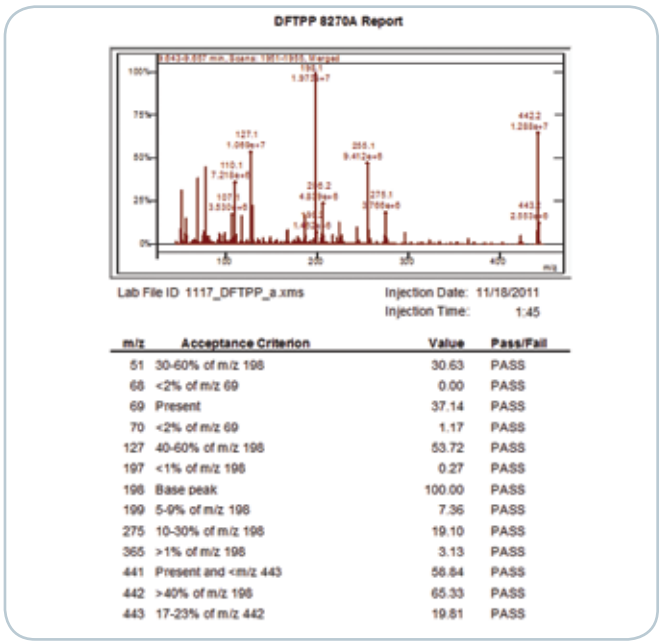

Figure 4: Peak tailing factor and Peak Gaussian report generated for the SPCC sample in Scion MSWS 8 Custom

Access reports

The other SPCCs are listed below in Table 2 as average RRF compared to the method 8270 criteria.

Compound	Method 8270 Criteria (Min RRF)	RRF on Scion SQ Cal Range 0.075-30ppm
N-nitroso-di-n-propylamine	0.05	0.109
Hexachlorocyclopentadiene	0.05	0.138
2,4-Dinitrophenol	0.05	0.149
4-Nitrophenol	0.05	1.03

Table 2: SPCC Results

After the system checks out a calibration series is analysed. In this case, the laboratory required a much lower concentration range than suggested by the method, from 0.075 ppm to 30 ppm (Method uses 5 ppm to 200 ppm). These concentrations clearly challenge the analytical system, especially for compounds that tend to be absorbed by active sites at low concentration. Figure 5 is an example section of a chromatogram in full scan mode for the calibration standard at 0.075 ppm. Internal standards are at a concentration of 40 ppm as recommended by the method. Note that the trichlorophenols are easily detected in scan mode.

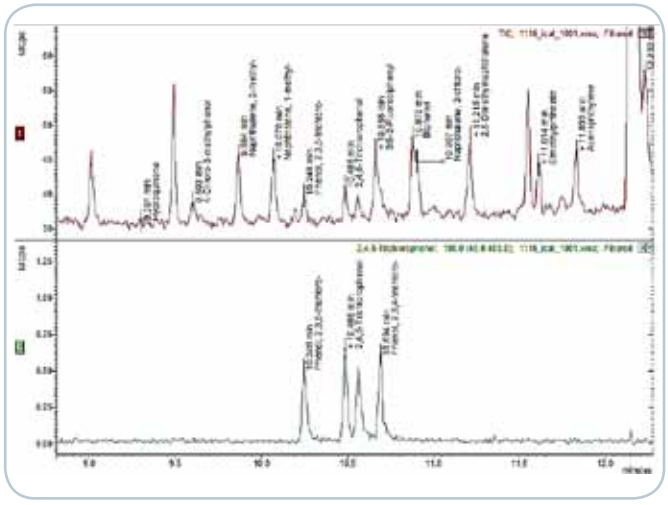

Figure 5: Full Scan of 0.075 ppm calibration standard (Top) and extracted ion chromatogram (bottom) for the trichlorophenols

Calibration curves for most analytes were linear over the calibration range, even for difficult compounds like pyridine as shown below. As seen here, the Scion SQ is a very inert system as there is no loss of the pyridine at the low end of the calibration curve.

Overall Calibration Statistics:
Average % RSD = 11.62 %
Average Correlation Coeffiecient =0.9989

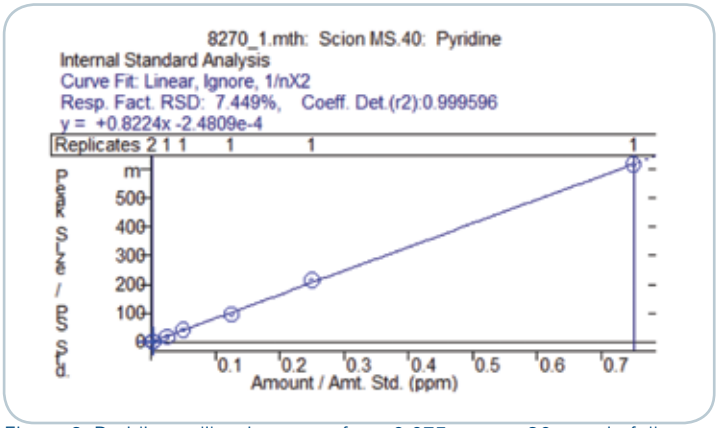

Figure 6: Pyridine calibration curve from 0.075 ppm to 30 ppm in full scan of the Scion SQ.

In order to gain even more sensitivity for key target compounds in Method 8270, SIM mode is often used. Modern GC/MS systems can be set up in a mixed scan mode, in which SIM ions are monitored at the same time during a full scan acquisition. The Scion SQ has a unique software feature known as Compound Based Scanning (CBS), in which SIM ions for compounds are stored in either a factory supplied library or user created library. The scan information, compound retention times, and individual dwell times are all stored and are easily selected and loaded directly into a data acquisition method.

CBS automatically optimizes scan times based upon desired number of data points to be acquired for a chromatographic peak, typically 10 points, so that accurate and precise quantitation is possible. The user does not have to manage complex time segments, because CBS automatically optimizes SIM scans throughout the chromatographic run based upon the retention time and retention time window. See Figure 7.

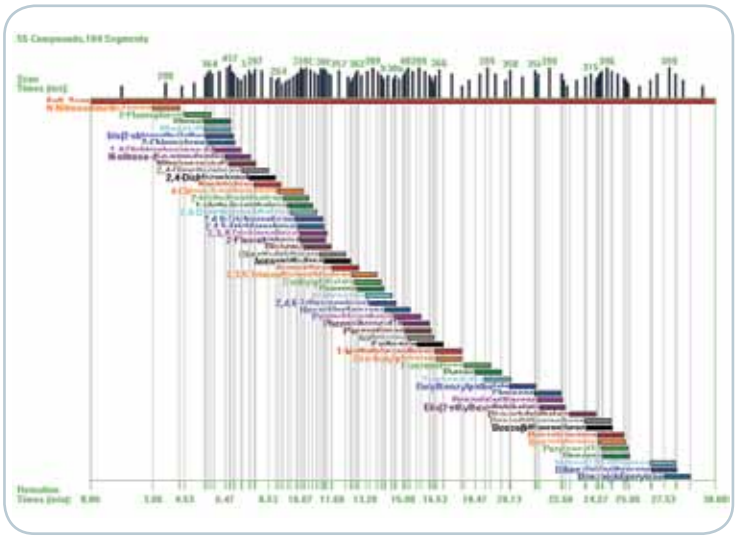

Figure 7: Mixed mode data acquisition for Method 8270. CBS automatically optimizes scanning ranges for target SIM ions. The full scan segment (red and on top) occurs throughout the run. The total scan time is represented by a bar graph at the top.

Conclusion

The Scion SQ GC/MS and MSWS software has been shown to be a complete solution for USEPA Method 8270. The robust ion source and sensitivity of the instrument allow for lower reporting limits in challenging sample extracts.

Compound based scanning is a novel approach allowing easy set-up and management of complex mixed mode methods. Compound scan information is loaded directly into the method by choosing them from a factory or user created library. It automatically optimizes scan times for SIM ions, and links the mass spectrometer acquisition table directly with data handling parameters, saving time and making it easier to add or delete compounds.

Standard EPA templates for Method 8270 and several other EPA methods are available in EnivroPro™, a Microsoft Access database reporting package.

Figure 10: The Scion EnviroPro™ software package for environmental methods in Microsoft Access 2010.

Instrumentation & Software
Scion SQ
451-GC
436-GC
8400 A/S

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