Application Note #1820229

GC/MS Linear Calibration with Extended Dynamic Range (EDR) Technology for ASTM D5769

Introduction

ASTM D5769 [1] is a method used commonly in refineries to quantify volatile organic compounds in gasoline. This can be a problem for GC/MS systems, because the analysis involves a wide range of volatile components at very high concentrations. The detector can easily become saturated and non-linear curves result. Modifying MS tuning conditions, ion source hardware, or electron multiplier settings during the run have been proposed ways of dealing with this problem.

However, such modifications involve more complexity in method setup for routine testing labs.

The SCION™ GC-MS uses a patented detection technology known as Extended Dynamic Range or EDR. EDR senses the level of the ion signal every scan and then adjusts the detector voltage and the perceived gain in order to keep the signal output at the optimum level for detection. This results in meeting the method linear calibration criteria without operator intervention or changes to the method procedure.

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Keywords	Instrumentation and Software
ASTM D5769	SCION Select SQ
Volatile Organic Chemicals (VOCs)	SCION 436-GC
Petrochemical	CP-8400 Autosampler
Gasoline	MSWS 8 Software
Extended Dynamic Range	
Refineries	

Experimental

The recommended instrument and operating parameters are listed in Table 1.

Table 1: Gas Chromatograph and Mass Spectrometer Conditions.

Gas Chromatograph	SCION 436
Inlet	SSL (Split/Splitless)
Mode	Split Injection, 0.1 µL
Injection Temp	250 °C
Pressure Pulse	None
Split Ratio	500:1
Inlet Liner	4 mm ID Split liner w/Frit, p/n RT233305

Oven

Oven Ramp	**°C/min**	**Temp °C**	**Hold (min)**
Initial		60	0.5
Ramp 1	3.0	120	1.0
Ramp 2	10	250	1.0
Total Run Time:		**35.5 min**	

Column

Scion BR-1ms, 60 m x 0.25 mm x 1.0 µm,p/n BR86644

Constant Flow 1.0 mL/min

Mass Spectrometer	SCION Select SQ
Solvent Delay	4 minutes
Scan Range	45-300 da
Dwell Time	250 ms
Ion Source Temp	250 °C
Transfer line Temp	280 °C
Detector	EDR

Calibration standards were obtained from AccuStandard Corporation, New Haven, CT, Gasoline Refinery Aromatics Standard, p/n D-5769-CAL/IS SET. The calibration levels were prepared based on the weight fraction found in refined gasoline as referenced in ASTM D5769.
A mass fragmentation pattern standard was also obtained to check for expected ion ratios for 1,3,5-Trimethylbenzene.

The advantage of EDR technology is that it makes automatic adjustments of the electron multiplier gain 'on the fly', in real time. If the signal is very large, the detector voltage goes down to avoid saturation. If the signal is small, the voltage goes up, so it efficiently detects low signal levels. Other MS detectors are set at a single voltage and must be manually adjusted to avoid saturation. If set too low, smaller signals are missed, and if set too high, the detector will saturate. In this case, methods must be set up with multiple segments making method development more complex.

Figure 1 is a representation of how EDR adjusts the detector gain as a peak elutes from the GC and ions arrive at the detector. Figure 2 shows the linear range of the detector for OFN, from a concentration on-column of 0.1 pg to 100 ng. Without EDR turned on, peaks will have the characteristic 'flat top' indicating saturation and result in poor quantitation. The mass spectrum also becomes distorted, resulting in poor qualitative identification in library searches.

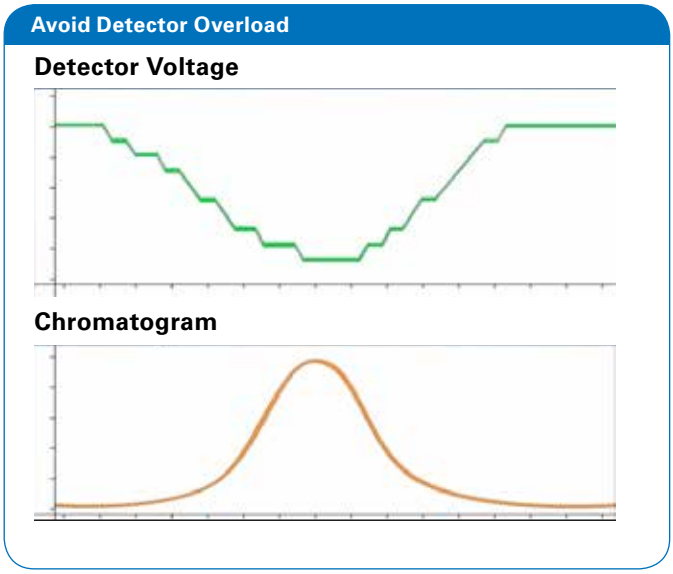


Figure 1: EDR automatically adjusts electron multiplier voltage in real time as peak elutes from the gas chromatograph, preventing detector saturation.

EDR: Extended Dynamic Range

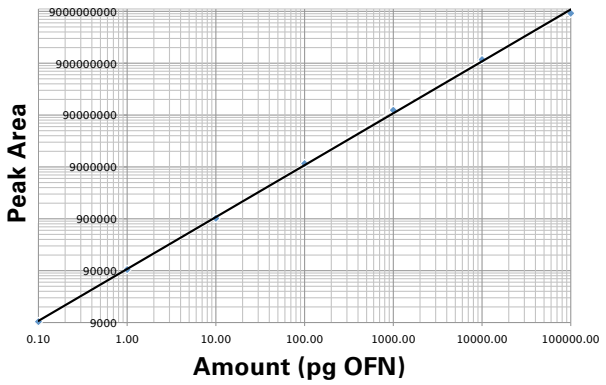


Figure 2: The linear range of the detector with EDR is demonstrated by injection of OFN from 0.1 pg to 100 ng on-column.

Results

The SCION GC-MS system was set up for ASTM D5769 and shown to easily meet the requirements for the mass fragmentation pattern standard and resolution. Built-in reporting tools help routine labs check this quickly as can be seen in Figures 3a and 3b.

Resolution Reports with Microsoft Access Quick-EP

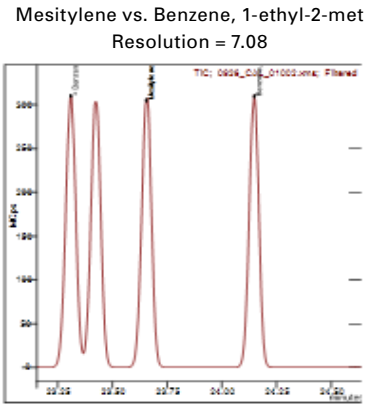
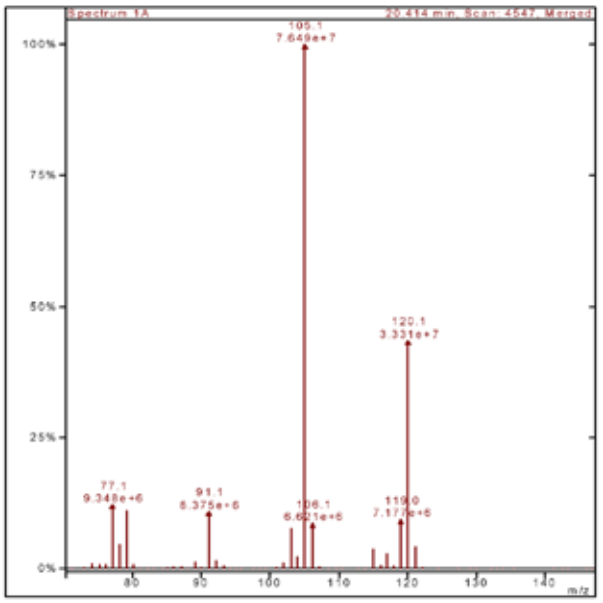


Figure 3a: Example report for 1,3,5-Trimethylbenzene (Mesitylene) and 1-Methyl-2-ethylbenzene.

Mass Fragmentation Pattern



Ion (m/z)	Acceptance Criteria	Observed Value
120	30-60	43
105	100	100
91	7-15	10.5

Figure 3b: Ion abundance requirement is easily met with the SCION Select SQ.

The calibration standards contain 23 volatile organics commonly found in gasoline. The ASTM method requires a 5 point calibration and if linear fits are used, the curves must have r^2 values greater than 0.99 and maximum of 5% RSD of response factors. All of the compounds were found to be linear over their respective ranges, with average % RSDs for all curves at 2.6% with average r^2 value of 0.9993.

Toluene has the highest concentration range and can easily saturate most MS detectors, even with split ratios greater than 1000:1. The SCION Select SQ maintains good linearity and mass spectral quality at the highest concentration standard as demonstrated in Figures 4a and 4b.

Toluene Calibration Curve

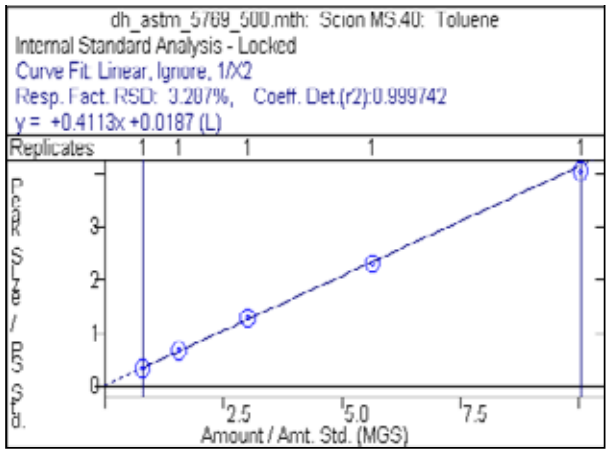


Figure 4a: Toluene not saturated at Level 01 (High Level) with linear curve on SCION SQ.

Toluene Mass Spectrum

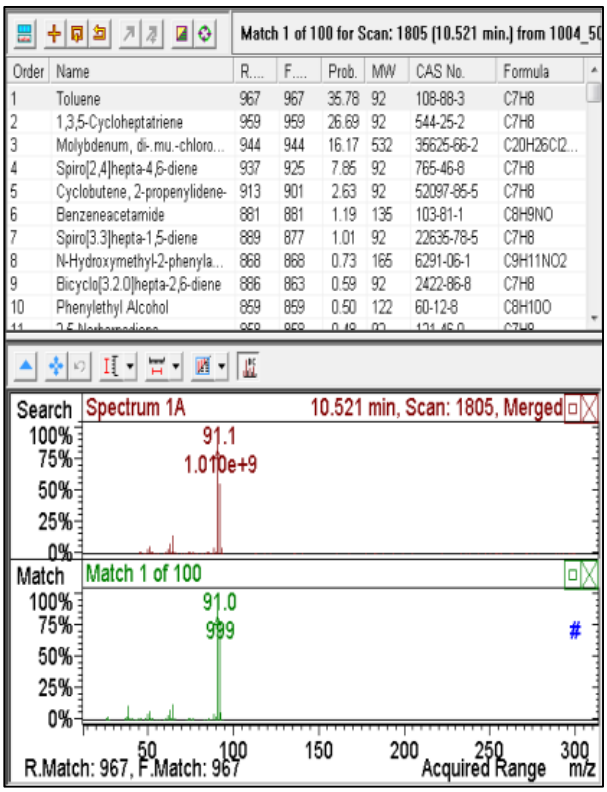


Figure 4b: Mass spectrum at apex of highest level standard shows no saturation and excellent spectral match vs. NIST library.

Conclusion

SCION GC-MS systems with EDR technology will extend the linear range of the mass spectrometer without requiring special modifications to the ion source hardware, MS tuning, or need for manual detector gain programming. EDR detects the ion signal and adjusts the gain in real time in order to avoid saturation. This makes method development easier for methods such as ASTM D5769 that require a wide dynamic range for volatile organics in gasoline.

References

[1] ASTM D 5769-04, Standard Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasoline by Gas Chromatography/Mass Spectrometry

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