Application Note

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Equimolar Response to ASTM D5623 Relevant Sulfur Compounds

Using an Agilent 8890 gas chromatograph and 8355 sulfur chemiluminescence detector (GC/SCD)

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Abstract

The petroleum industry requires the measurement of low levels of sulfur in a product, which may be difficult as sulfur can be present in a range of quantities and exist as various compounds within the distillation process. This application note offers a method for the precise determination of sulfur compounds with equimolar response using an Agilent 8355 sulfur chemiluminescence detector (SCD). Excellent area reproducibility and linearity were achieved, with the area percent relative standard deviation (%RSD) values under 5% for all compounds and correlation coefficients (R^2) > 0.9999 for tert-butyl disulfide. This method demonstrates the equimolar response of similar analytes to those listed in the ASTM International D5623 Standard Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection (ASTM D5623). When the SCD is used in tandem with a flame ionization detector (FID), the method can also be used to monitor the elution process and identify potential peak interferences.

Introduction

For many years, the use of a sulfur-specific detector in the petroleum industry has been invaluable for accurately identifying low levels of sulfur-containing compounds in petroleum at various stages of production.[1] Many environmental and health requirements limit the amount of sulfur allowed in the final petroleum product. The presence of sulfur also has the potential to poison the catalytic processes that take place during petroleum refining.

Along with the determination of low sulfur levels in a petroleum sample, a detector may also need to measure high sulfur levels and total sulfur content. A detector with a high linear range is essential in making both low-level and high-level determinations of sulfur in a petroleum sample.

In this application note, an Agilent 8355 SCD was used to measure 19 sulfur-containing compounds within a standard sample. The 8355 SCD is ideal for the widely used ASTM D5623 method[2] because of its ability to obtain linear and equimolar responses to sulfur compounds with minimal hydrocarbon interference. When comparing the equimolar response of analytes containing different numbers of sulfur atoms, the response should be double for the analytes containing two sulfur atoms compared to those with one sulfur atom.

Another advantage of the 8355 SCD is the ability to use it in tandem with an FID. This combination allows monitoring solvent elution through the GC system, assisting in the detection of the coelution of solvents with analyte peaks. These coelutions can cause peak distortion, which might be mistaken for activity issues within the GC system.

Methods

Instrumentation

Two Agilent 8890 GC systems were equipped with an 8355 SCD. Both GC/SCD systems were run in the same manner to confirm equimolar results. A third GC system was also configured with a tandem flame ionization detector sulfur chemiluminescence detector (FID/SCD) to allow the determination of the solvent peak elution from the system. This third system also served as another confirmation of the equimolar results that were obtained from the other two GC/SCD systems. Sample introduction for all systems was completed with an Agilent 7693A automatic liquid sampler with a 5 µL syringe. The sample volume for each injection was 1.0 µL. All analyses were performed with a split/splitless inlet in split mode.

The GC/SCD parameters are provided in Table 1. Note that an Agilent DB-Sulfur SCD GC column (part number G3903-63002) was used in this study because of the low column bleed and excellent inertness and performance for sulfur compound analysis. When using the SCD, be aware that stationary phase bleed from the GC column can lead to fouling of the ceramic tubes within the detector. This phenomenon can cause poor SCD performance, such as decreased sensitivity, and may require more frequent maintenance. Proper GC column selection (such as the DB-Sulfur column) is important to ensure lower column bleed into the detector and will reduce fouling of ceramic tubes, reducing instrument downtime.

Table 1. GC/SCD acquisition parameters.

Parameter	Value
Column	Agilent J&W DB-Sulfur SCD, 40 m × 0.32 mm, 0.75 µm (p/n G3903-63002)
Carrier	Helium, constant flow, 3.5 mL/min (54 cm/s)
Oven	40 °C (1 min), 10 °C/min to 170°C (hold 10 min) Run time: 24 min
Inlet	S/SL, Split mode, 250 °C, split ratio 200:1 for standard SCD and 100:1 for FID SCD system
Inlet Liner	Agilent Ultra Inert, split, low pressure drop, glass wool (p/n 5190-2295)
SCD	Base: 280 °C Burner: 800 °C Upper H_2 flow: 35 mL/min Lower H_2 flow: 12 mL/min Oxidizer flow (air): 60 mL/min
FID-SCD	**FID** Temperature: 350 °C H_2 flow: 35 mL/min Air flow: 500 mL/min Makeup flow (N_2): 20 mL/min **SCD** Base: 250 °C Burner: 800 °C Upper H_2 flow: 40 mL/min Oxidizer flow (air): 5 mL/min

Standard preparation and analysis

An in-house solution of 19 sulfur-containing compounds was prepared in isooctane at 50 ppm for the equimolar study (Table 2). A variety of sulfur-containing analytes with one, two, and three sulfur atoms per molecule were used. Stock solutions of each compound were made in isooctane using neat standards obtained from Sigma-Aldrich Corporation as well as individual solutions at 2,000 ppm in toluene from AccuStandard. Figure 1 shows an example chromatogram of the 19-analyte mixture that was used in the in-house sulfur mix.

Table 2. 19-Sulfur containing analytes test mixture.

No.	Analyte	CAS No.	No. Sulfur Atoms
1	Ethanethiol	75-08-1	1
2	Dimethyl sulfide	75-18-3	1
3	Carbon disulfide	75-15-0	2
4	2-Propanethiol	75-33-2	1
5	tert-Butylthiol	75-66-1	1
6	1-Propanethiol	107-03-9	1
7	Ethyl methyl sulfide	624-89-5	1
8	Thiophene	110-02-1	1
9	2-Methyl-1-propanethiol	513-44-0	1
10	Diethyl sulfide	352-93-2	1
11	1-Butanethiol (ISTD)	109-79-5	1
12	Dimethyl disulfide	624-92-0	2
13	2-Methylthiophene	554-14-3	1
14	3-Methylthiophene	616-44-4	1
15	Diethyl disulfide	110-81-6	2
16	Dimethyl trisulfide	3658-80-8	3
17	5-Methylbenzo(b)thiophene	14315-14-1	1
18	3-Methylbenzothiophene	1455-18-1	1
19	Diphenyl sulfide	139-66-2	1

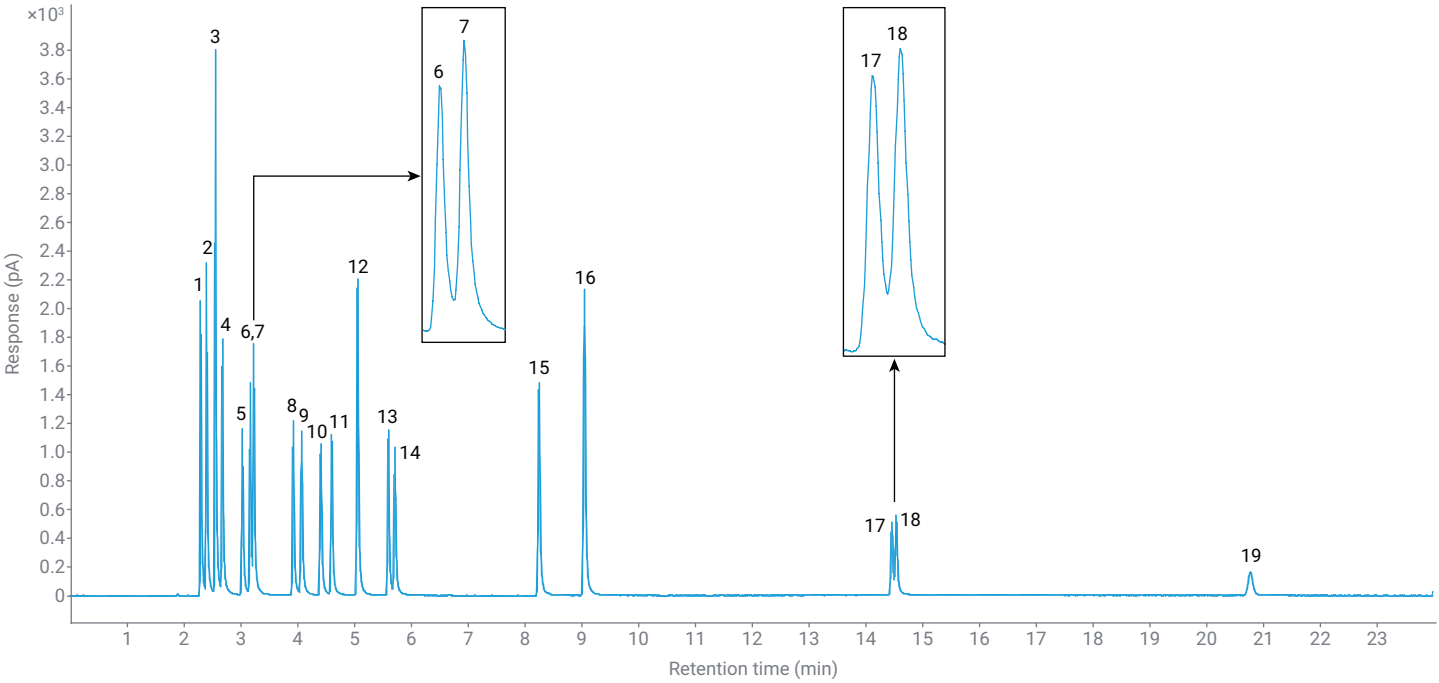

Figure 1. Chromatogram of the 19-analyte mixture used in the sulfur samples. The zoomed-in images show peaks "6, 7" and "17, 18" to demonstrate the separation of the pairs.

Results and discussion

Use of GC/FID for solvent elution determination

Determination of the solvent peak elution can be a challenge when using a sulfur-selective detector such as the SCD. Many times, the large, fronting solvent peak may coelute with analytes of interest, causing distortion of the analyte peak shape (peak tailing, fronting, or broadening) and poor chromatographic separation. This poor peak shape, caused by column overloading, can be mistaken for activity issues in the system or hydrocarbon interferences, leading to unnecessary troubleshooting or inlet/column maintenance. Determination of the solvent peak elution time is recommended to ensure that coelution does not occur with any of the analytes of interest.

To confirm the solvent elution time, a tandem GC/FID/SCD system was used. The GC/FID/SCD system puts the FID in-line before the SCD analysis, allowing the user to obtain both FID and SCD signals from a single injection, thus confirming the solvent retention time and determining any solvent/analyte coelutions.

Figure 2 shows the zoomed-in and overlaid chromatograms from the GC/FID/SCD system for peaks 8 to 14 and the coeluting solvent (isooctane). The purple trace shows the FID signal, and the orange trace shows the SCD signal. As shown in Figure 2, analyte coelution with the solvent can drastically distort the analyte peak shape due to the column overload of the solvent. Specifically, the analytes diethyl sulfide (peak 10) and 1-butanethiol (peak 11) demonstrate how coelution with isooctane through the GC system caused peak distortion and broadening.

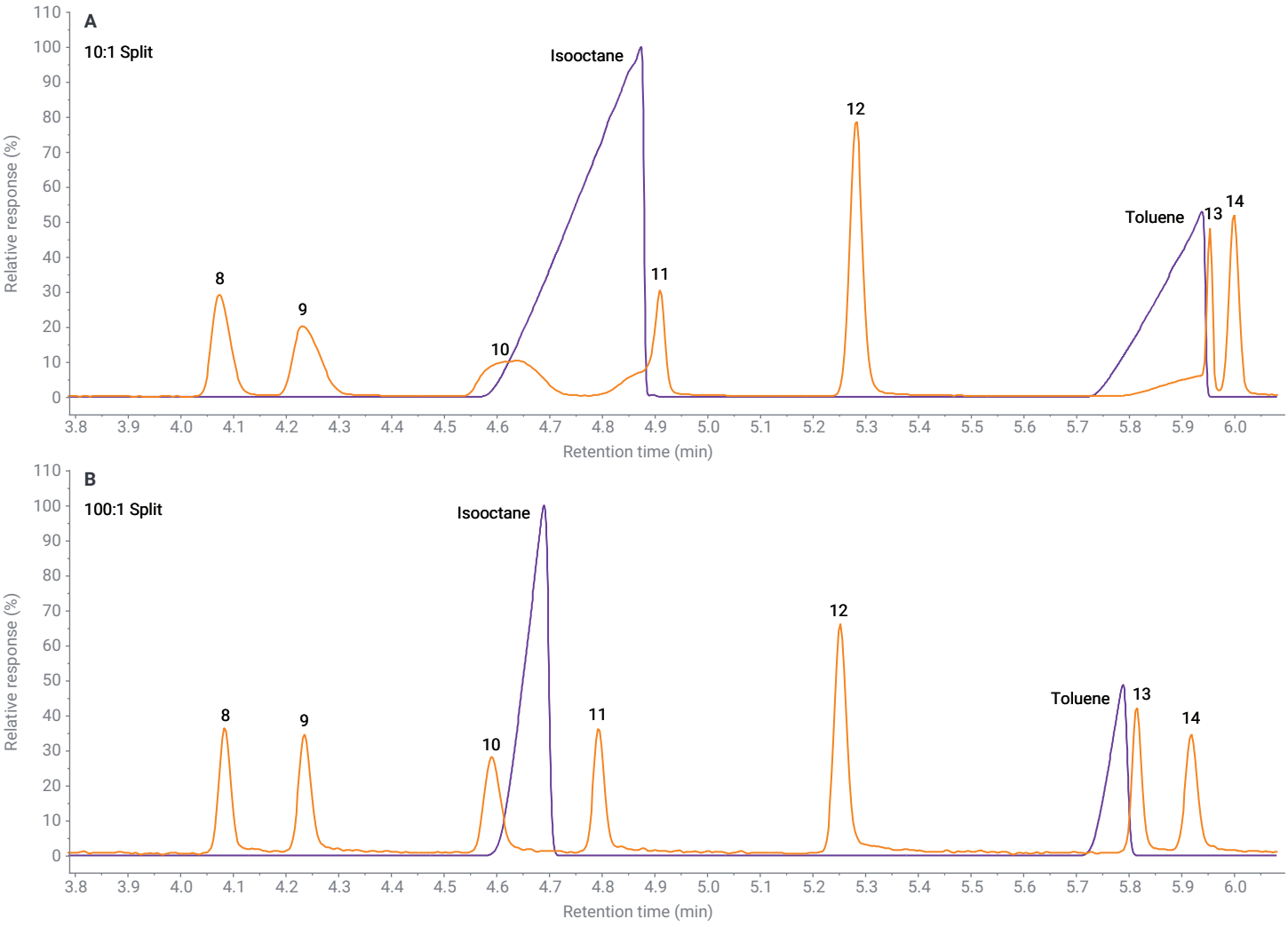

Figure 2. (A) Chromatogram with FID and SCD signals overlaid showing peaks 8 to 14 and solvents, 10:1 inlet split. (B) Chromatogram with FID and SCD signals overlaid showing peaks 8 to 14 and solvents, 100:1 inlet split.

The peak shape of 3-methylthiophene (peak 13) also shows signs of distortion as it coelutes with the tail end of the toluene solvent peak (toluene was present as the original solvent in many of the purchased standards although the final stock solution was diluted in isooctane).

To minimize the distortion effect of the solvent peak coelution, the inlet split ratio was increased from 10 (Figure 2A) to 100 (Figure 2B). Increasing the split ratio reduced the amount of solvent introduced in the system, leading to more narrow peaks. The use of a higher split ratio does improve the peak shape of the coeluting analytes, but peak distortion was not completely removed. Because of this improved analyte peak shape, the higher split ratio was used in further analysis.

Use of the DB-Sulfur SCD GC column

For the equimolar study, a DB-Sulfur SCD GC column was chosen because of the requirement for minimal column bleed into the SCD. Minimizing the column bleed is required for obtaining reproducible and sensitive results when using the SCD. Excess column bleed can foul the ceramics that are used within the SCD burner, causing poor results ranging from sensitivity issues to higher area reproducibility. Use of a DB-Sulfur SCD GC column also provides excellent peak shape for sulfur-containing analytes, including many of those found in the ASTM D5623 application.

Area reproducibility

Obtaining good area reproducibility is a must for all analytical instrumentation. Table 3 demonstrates how an Agilent 8355 SCD easily provides this with the analytes of interest for the ASTM D5623 application. All the results are well below the 5% area relative standard deviation (RSD) specifications for the 8355, n = 7 for each GC tested.

Linearity

The Agilent 8355 SCD provides linearity for the detection of sulfur compounds over a range of at least 10^4. Figure 3 shows the sulfur concentration calibration plots for tert-butyl disulfide over the concentration range of approximately 0.5 to 10,000 pg/µL S (specifically 0.5034 to 10,280) on GC/SCD 1 and 2. Tert-butyl disulfide is the analyte used for the 8355 SCD linearity specification and was chosen to demonstrate linearity representative of the 19 analytes evaluated. As seen in Figure 3, good R^2 values of > 0.9999 were obtained over this concentration range for both SCD units.

Table 3. Area %RSD for 19 sulfur-containing analytes of interest by GC system tested.

No.	Compound	SCD 1 (%)	SCD 2 (%)	FID/SCD (%)
1	Ethanethiol	2.24	2.93	1.95
2	Dimethyl sulfide	2.51	2.45	1.83
3	Carbon disulfide	2.74	1.83	1.61
4	2-Propanethiol	2.09	2.48	2.07
5	tert-Butylthiol	1.29	1.87	2.72
6	1-Propanethiol	1.07	2.32	1.28
7	Ethyl methyl sulfide	2.41	2.40	1.49
8	Thiophene	2.33	2.13	2.94
9	2-Methyl-1-propanethiol	2.56	3.36	2.71
10	Diethyl sulfide	1.50	2.71	2.28
11	1-Butanethiol	1.97	2.58	2.89
12	Dimethyl disulfide	1.93	1.55	1.67
13	2-Methylthiophene	1.65	1.04	2.81
14	3-Methylthiophene	2.16	1.93	3.45
15	Diethyl disulfide	1.35	1.85	1.87
16	Dimethyl trisulfide	1.77	1.99	1.00
17	5-Methylbenzo(b)thiophene	0.43	1.58	2.96
18	3-Methylbenzothiophene	2.10	2.05	2.03
19	Diphenyl sulfide	1.51	2.81	3.42

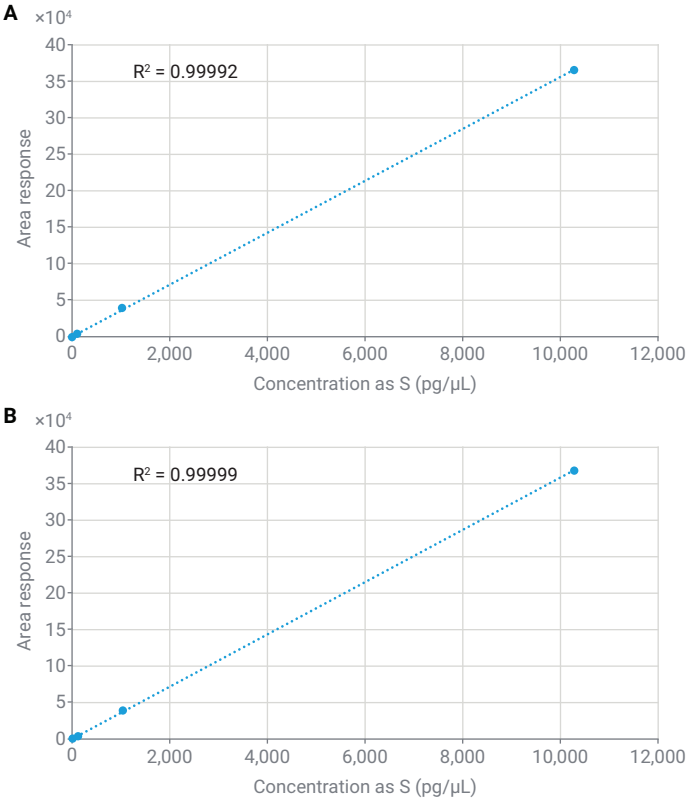

Figure 3. Calibration plots for tert-butyl disulfide on two GC/SCD systems, (A) GC/SCD 1, (B) GC/SCD 2.

Equimolar response

The Agilent 8355 SCD provides an equimolar response for sulfur-containing analytes, demonstrated with 19 compounds relevant to the D5623 application. Results from three different SCD burners were evaluated for this study (two standalone SCDs and one FID/SCD).

Determination of equimolar results can be calculated by a variety of different metrics. The relative molar sensitivity (RMS) calculation was used for the analytes of interest for this application note. Equation 1 shows the RMS calculation.

Equation 1.

$$RMS = \frac{(\text{Average peak area analyte})/(\text{mol number analyte})}{(\text{Average peak area ISTD})/(\text{mol number ISTD})}$$

The compound 1-butanethiol, which contains a single sulfur atom, was used as an internal standard (ISTD) in the RMS calculation. In an equimolar system, the RMS values should be close to the number of sulfur atoms in the molecule.

Table 4 shows the 19 ASTM D5623 analyte results for three SCD burners (over two GC systems). As shown in Table 4, all the analytes of interest show the correct equimolar response with respect to the number of sulfur atoms present.

Table 4. RMS values for the ASTM D5623 analyte test results over three SCD burners.

No.	Analyte	No. Sulfur Atoms	SCD 1	SCD 2	FID/SCD	Average	Standard Deviation	%RSD
1	Ethanethiol	1	0.88	0.72	0.82	0.81	0.081	10.0
2	Dimethyl sulfide	1	1.01	0.88	0.95	0.95	0.065	6.9
3	Carbon disulfide	2	1.97	1.89	1.84	1.90	0.066	3.4
4	2-Propanethiol	1	1.10	1.01	1.01	1.04	0.052	5.0
5	tert-Butylthiol	1	0.96	0.90	0.98	0.95	0.042	4.4
6	1-Propanethiol	1	0.88	0.87	0.92	0.89	0.026	3.0
7	Ethyl methyl sulfide	1	1.18	1.10	1.12	1.13	0.042	3.7
8	Thiophene	1	0.96	0.94	0.99	0.96	0.025	2.6
9	2-Methyl-1-propanethiol	1	1.06	1.04	1.04	1.05	0.012	1.1
10	Diethyl sulfide	1	1.05	1.05	1.10	1.07	0.029	2.7
11	1-Butanethiol (ISTD)	1	–	–	–	–	–	–
12	Dimethyl disulfide	2	2.14	2.13	2.12	2.13	0.010	0.5
13	2-Methylthiophene	1	1.01	1.03	1.07	1.04	0.031	3.0
14	3-Methylthiophene	1	1.07	1.08	1.11	1.09	0.021	1.9
15	Diethyl disulfide	2	2.12	2.13	2.25	2.17	0.072	3.3
16	Dimethyl trisulfide	3	3.20	3.13	3.24	3.19	0.056	1.7
17	5-Methylbenzo(b)thiophene	1	0.90	0.89	1.18	0.99	0.165	16.6
18	3-Methylbenzothiophene	1	1.09	1.10	1.26	1.15	0.095	8.3
19	Diphenyl sulfide	1	0.85	0.94	1.11	0.97	0.132	13.7

Conclusion

The Agilent 8355 sulfur chemiluminescence detector, paired with an Agilent 8890 GC, was evaluated by analyzing 19 sulfur-containing compounds relevant to ASTM D5623. The SCD met the specifications of the test method, including an equimolar response to the analyzed sulfur compounds and a wide range of linearity to a sulfur-containing standard. The 8355 SCD shows excellent area reproducibility, and when used in tandem with a flame ionization detector, the system can aid in the determination of solvent peak elution through the GC system.

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DE-008905

Printed in the USA, August 15, 2025
5994-8562EN

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