

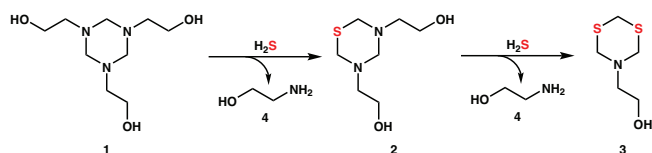
## APPLICATION NOTE

# The application of benchtop NMR for investigating the performance of H<sub>2</sub>S scavengers

Based on previously published work: Brown, B. A. *Magn. Reson. Chem.* **2020**, 58, 1249-1255



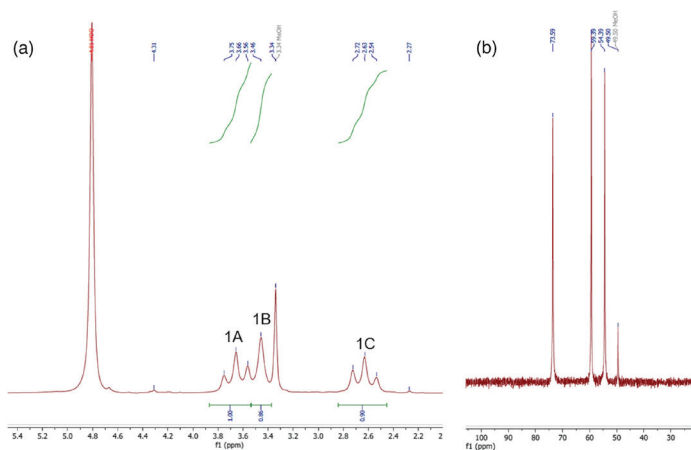
Hydrogen sulfide is commonly found in natural gas and can be fatal at very low concentrations.<sup>2,3</sup> Commonly, this product is sequestered using H<sub>2</sub>S scavengers, such as triazines.<sup>4</sup> A common reaction pathway is shown in **Figure 1**, wherein triazine **1** sequentially reacts with two equivalents of H<sub>2</sub>S to form **3** via intermediate **2**.<sup>5</sup> Under the right conditions, the two equivalents of monoethanolamine (MEA, **4**) formed during these transformations can further react with H<sub>2</sub>S.<sup>6</sup>



**Figure 1.** Triazine (**1**) reaction pathway with H<sub>2</sub>S to sequentially form thiadiazine (**2**) and dithiazine (**3**), along with two equivalents of MEA (**4**).

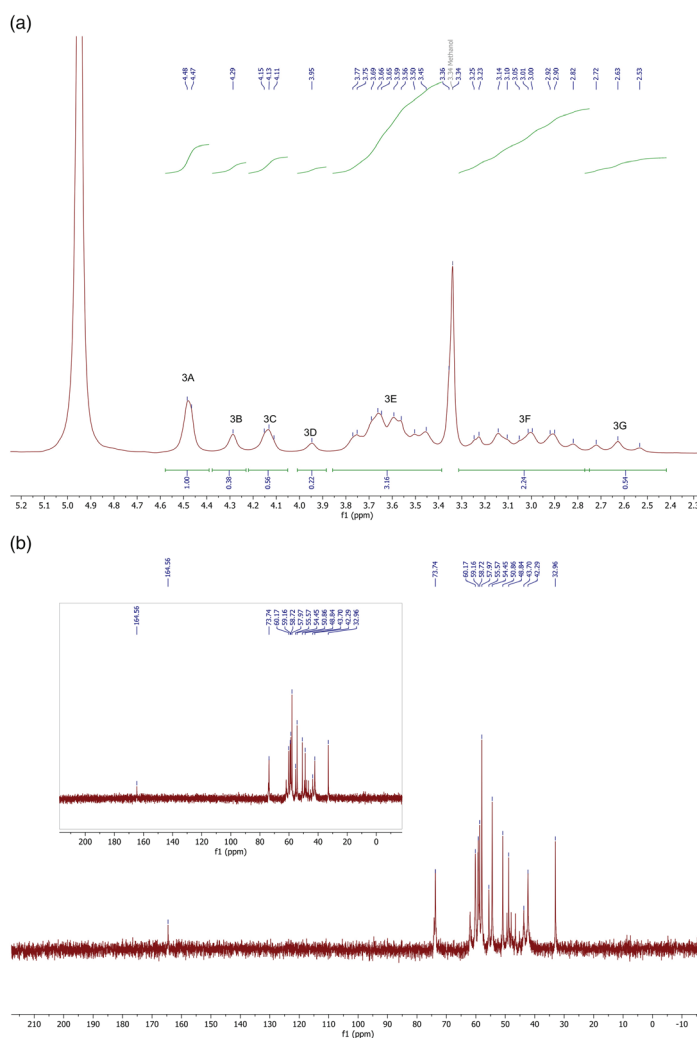
As the scavenger (**1**) gets overspent, the formation of solid deposits of dithiazine (**3**) can cause a myriad of issues, leading to the need for characterization of the products of this reaction to determine the remaining scavenging capacity of the triazine (**1**).<sup>7</sup> Raman spectroscopy has been used to successfully monitor these transformations,<sup>8</sup> but nuclear magnetic resonance (NMR) remains an underutilized technique for these analyses. While the products of these reactions are well-characterized by NMR,<sup>9</sup> the high upfront and recurring costs of traditional high-field instruments, coupled with their size and requirements for expert staff to maintain and operate, means these instruments are challenging to incorporate in most industries. The rise in popularity and performance of high-resolution benchtop NMR spectrometers has made this technique accessible to more laboratories than ever, making it ideal to monitor these types of transformations.

In this study published by Brown,<sup>1</sup> one unspent scavenger (**1**) and four spent scavengers (obtained from the field) were studied using <sup>1</sup>H and <sup>13</sup>C NMR. Controlled exposure to H<sub>2</sub>S also allowed to characterize its reactivity with the scavenger over time. The spectra for **1** are shown in **Figure 2**. The expected resonances are obtained in both spectra, providing a useful base from which to compare reaction products.



**Figure 2.** <sup>1</sup>H (60 MHz, left) and <sup>13</sup>C (15 MHz, right) NMR spectra of triazine (**1**) in CD<sub>3</sub>OD.<sup>1</sup>

The noticeably more complex <sup>1</sup>H spectrum for spent scavenger is shown in **Figure 3a** (top), while the <sup>13</sup>C spectrum appears in **Figure 3b** (bottom).

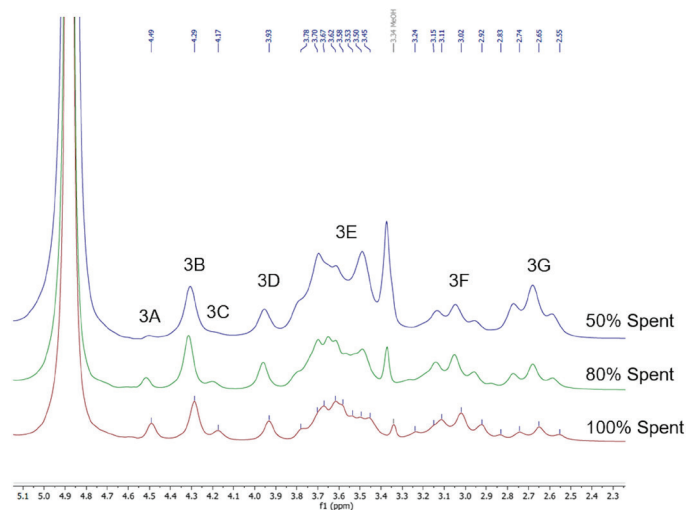


**Figure 3.** <sup>1</sup>H (60 MHz, top) and <sup>13</sup>C (15 MHz, bottom) NMR spectra of spent scavenger in CD<sub>3</sub>OD.<sup>1</sup>

The signals labeled as 3A and 3C in **Figure 3a** were assigned to the N-CH<sub>2</sub>-S and S-CH<sub>2</sub>-S resonances in dithiazine (**3**), respectively. The presence of this species was also confirmed using the peak at 32.96 ppm via <sup>13</sup>C, which was assigned to the S-CH<sub>2</sub>-S resonance. Additionally, signals 3B and 3D in the <sup>1</sup>H spectrum were assigned to the S-CH<sub>2</sub>-N and N-CH<sub>2</sub>-N resonances in thiadiazine (**2**), respectively. The presence of **2** was further confirmed using the peak at 73.7 ppm in **Figure 3b**, which was assigned to the N-CH<sub>2</sub>-N resonances. Furthermore, the relative integrations between these signals confirm that the thiadiazine (**2**) is the minor product compared to dithiazine (**3**). The presence of unreacted scavenger was confirmed using peaks 3G in the <sup>1</sup>H spectrum, and the peaks at 74.2 ppm, 59.3 ppm, and 54.5 in the <sup>13</sup>C spectrum, which all match those observed in **Figure 2**.

Studying the reactivity of the triazine (**1**) with varying amounts of H<sub>2</sub>S was performed by passing a mixture of gas through a pH-controlled solution of the scavenger and measuring the “break-through” time,

at which point the scavenger was deemed to be 100% spent. From these results, the experiments were repeated to prepare solutions of scavengers which were 80% and 50% spent. These results indicated that the spent scavenger samples looked almost identical to the samples obtained from the field, including the residual presence of **1**, indicating that it is not entirely consumed. Interestingly, the presence of **3** was minimal in the 50% spent solution, with only a small amount starting to appear in the 80% spent solution. Indeed, **3** only became a major reaction product once break-through had occurred. A stacked  $^1\text{H}$  NMR plot of the 50%, 80%, and 100% spent solutions is shown in Figure 4.



**Figure 4.** Stacked  $^1\text{H}$  NMR (60 MHz) plot of 50%, 80%, and 100% spent triazine (**1**) solutions exposed to  $\text{H}_2\text{S}$  in a controlled laboratory environment.<sup>1</sup>

These studies demonstrate that benchtop NMR can be used to monitor the reactivity of **1** towards  $\text{H}_2\text{S}$ . They also show that amounts of both **1** and **2** are still present at the break-through point, indicating that something else is inhibiting further reactivity.

This application note is a summary of work published by Brown in *Magnetic Resonance in Chemistry*.<sup>1</sup> For more information on the work discussed herein, the reader is encouraged to read the full publication.

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