SHIMADZU

Application News

Total Organic Carbon Analysis SSI-TOC-001

Analysis of Brine Solution with Shimadzu TOC-L Series Total Organic Carbon Analyzer

Robert H. Clifford, Ph.D. and Dan L. Davis, Shimadzu Scientific Instruments, USA
Kiyuki Noto, Shimadzu Corporation, Japan

Problem

Chlor-Alkali Chemistry utilizes brine solution (28% NaCl), which requires high maintenance on TOC analyzers.

Solution

Shimadzu's High Salt Kit (P/N 638-93176-01 & 638-93176-02) will allow 12 times more sample injections on to the catalyst before replacement and increase the quartz combustion tube life by a factor of five. This type of kit is available for laboratory TOC-L or on-line TOC-4110 (P/N 638-93176-00) analyzers.

Background

Normally, combustion type TOC analysis utilizes hydrochloric acid (HCl) as the preservative acid. The sample is pH adjusted to acidic conditions with a drop or two of HCl in the sample. However, for brine solutions (28% NaCl), the acid recommended is sulfuric acid (H2SO4). The H2SO4 is added not as a preservative, but to modify the matrix. By changing the matrix the maintenance is reduced with respect to the quartz combustion tube life. The chemistry is that NaCl melts at 801 °C and thus causes the quartz tube to go thru the decaying process of devitrification more quickly. Adding H2SO4 to NaCl produces HCl and Na2SO4, which melts at 881 °C; this degrades the quartz tube at a much slower rate. This reaction requires two Na^+ ions to react with each $SO4^{-2}$ ion. To maintain the stoichiometry of this reaction, the sulfate ion concentration (>14%) would need to be at least half of the sodium ion concentration (28%). Thus, in this experiment, the sulfuric acid concentration was set 1% higher to 15%, which results in longer combustion tube life.

Second, utilizing a wider diameter combustion tube has two effects: a) less contact of acid with the quartz combustion tube increases its lifetime, and b) allows higher levels of salt buildup and prevents blocking of the flow path, resulting in longer operation times. The combination of using H2SO4 and a wider diameter combustion tube results in an increase in the life of the combustion tube by approximately 5 times.

With the larger combustion tube, the TOC-L utilizes two types of catalyst: the normal catalyst and a larger diameter catalyst. There are a number of advantages that come from combining the two different catalysts. More catalysts results in a more active surface area for a longer life. The large catalyst allows easier flow of the carrier gas and CO2 reaction gas without clogging. Also, the quartz wool, which holds the catalyst in place, is replaced with a ceramic frit material that doesn't clog as easily. The result is 12 times more sample may be injected on to the catalyst before maintenance needs to be performed.

Experiment

Before the analysis a 0-10 ppm calibration curve was created with 50 uL injections of KHP solution. Then, the 0 ppm and 10 ppm standards were analyzed for concentration (dark blue) and area counts (magenta) as shown in Figure 1. After confirming the system was operating properly, a 5 ppm solution of KHP with a matrix of 28% NaCl was analyzed 110 times with very reproducible results. The 0 ppm and 10 ppm standards were analyzed again for accuracy and reproducibility. The procedure was repeated again after the system had run 220 injections of 5 ppm KHP with 28% NaCl matrix. Again, the 0 ppm and 10 ppm standards solutions were still very stable. More experiments need to be performed in order to test the limitations of the TOC-L to determine when maintenance is required.

Maintenance

It is recommended to use a wash bottle and rinse off the slider block at the end of each day. Figure 2a shows a picture of the normal slider before brine analysis, while figure 2b shows a picture of the slider with salt buildup after 220 injections of 28% NaCl. The rinse process was performed very easily and quickly. Figure 3 shows the top of the slide block which also should be cleaned daily when analyzing brine solutions because of salt buildup. Using a SO3 scrubber (P/N 220-95268-01) in-line before the standard halogen scrubber to protect the NDIR detector is also recommend.

Conclusion

TOC maintenance time and cost can be reduced significantly by using a high salt kit when analyzing brine solutions (28% NaCl). Results are very good over 220 samples containing brine. Future work includes how many samples can be analyzed before maintenance is required.

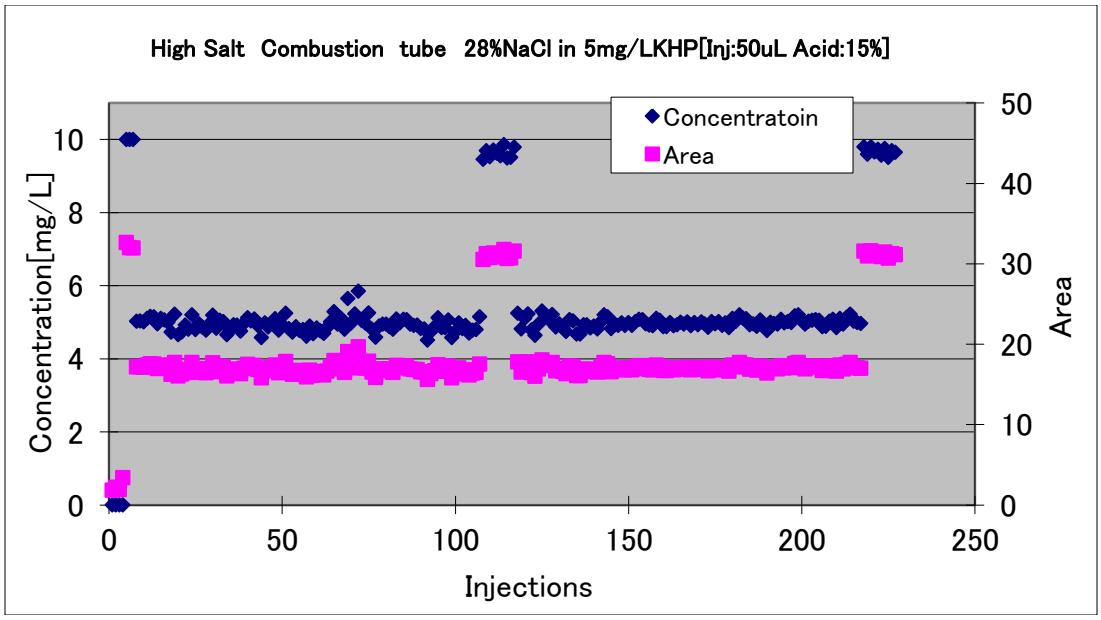

Figure 1: Analysis of 220 repetitions of 5 ppm in 28% NaCl and 15% H2SO4 matix. At 1, 110, and 220, a number of 0 and 10 ppm standards were analyzed.

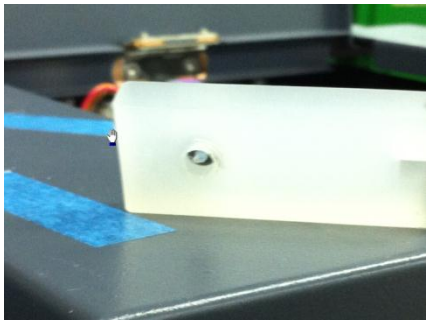

Figure 2a: TOC slider before analysis of brine solution (28% salt)

Figure 2b: TOC slider after analysis of brine solution (28% salt)

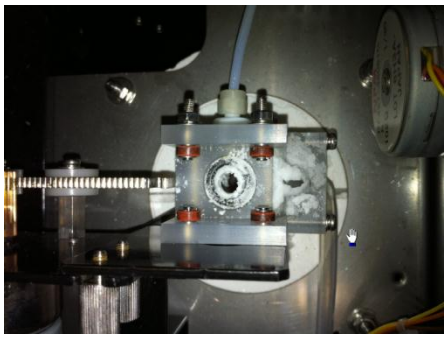

Figure 3: TOC slider block after analysis of brine solution (28% salt)

Shimadzu Scientific Instruments
7102 Riverwood Drive, Columbia, MD 21046
Phone: 800-477-1227, Fax: 410-381-1222
www.ssi.shimadzu.com
webmaster@shimadzu.com

Related Products Some products may be updated to newer models.

TOC-L Series
Total Organic Carbon Analyzer

Price Inquiry

Product Inquiry

Technical Service / Support Inquiry

Other Inquiry