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Automated Preparation of Viscous Vacuum Gas Oil Samples for Total Sulfur and Nitrogen Determination Using the Agilent 7696A Sample Prep WorkBench

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Introduction

The Agilent 7696A Sample Prep WorkBench is a versatile sample preparation platform capable of accurate and precise delivery of liquids directly into autosampler vials. The Sample Prep WorkBench can be equipped with a vial heater for heating samples up to 80 °C, a semi-microbalance (WeighStation) for precise mass measurements to five decimal places, a tray heater to heat vials to 60 °C, and a Peltier tray cooler to cool vials down to -5 °C.

In this study, the use of the Sample Prep WorkBench for transferring aliquots of viscous liquids is investigated. Techniques for optimizing accuracy and precision are explored using viscosity reference standards. In addition, the maximum viscosity that can be transferred within syringe precision is estimated. These techniques are applied to the preparation of a vacuum gas oil (VGO) samples for total sulfur and nitrogen determination. The strategies presented may be applied in the preparation of other viscous samples such as food and mineral oils.

Experimental

The Sample Prep WorkBench was used to prepare all samples in this study. It was equipped with a tray heater, vial heater and WeighStation. Poly-butene viscosity standards were purchased from Cannon Instrument Company (College Station, PA, USA). VGO samples were received from a petroleum refinery laboratory. VGO samples were diluted in toluene before total sulfur and nitrogen determination by gas chromatography with chemilumenenscence detection. Kinematic viscosity of the VGO sample was determined by ASTM D445 (Cannon Instrument Company).

Results

Viscosity Limit, Accuracy and Precision

Figure 1 shows the volume of 25 mL aliquots of the S200 standard delivered into 1 mL of toluene at different vial heater settings. The volume was determined based upon the mass of the S200 delivered into the toluene and the density at the time of aspiration. The black horizontal lines show the accuracy range for 25 mL aliquots delivered by a 100 µL syringe. The red vertical line was used to determine the maximum viscosity that could be transferred within the delivery accuracy of the syringe. Figure 2 and 3 show the corresponding precision and accuracy of the S200 standard based upon 5 replicates, respectively.

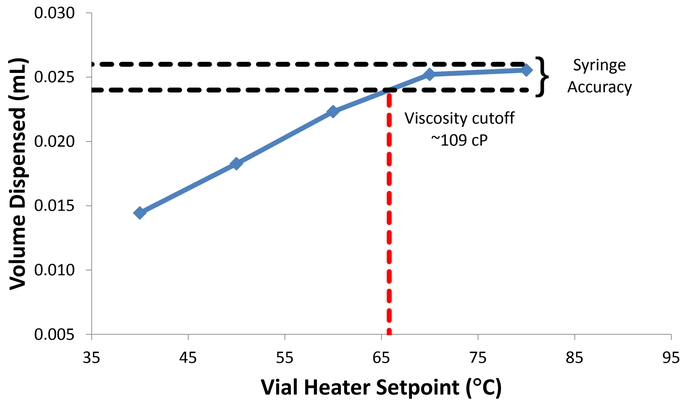

Figure 1. Volume of S200 dispensed at different vial heater settings

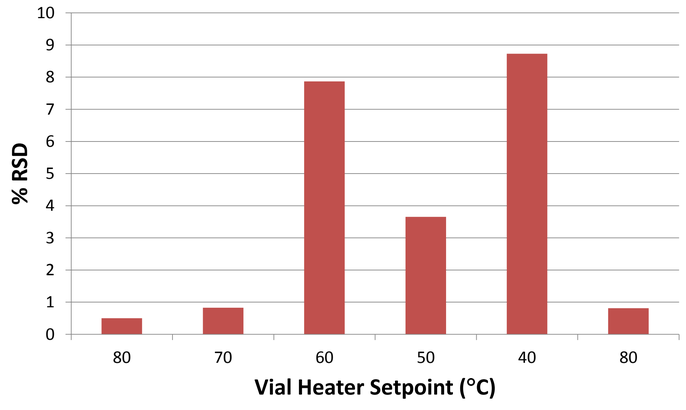

Figure 2. Precision of 25 mL aliquots of S200 dispensed

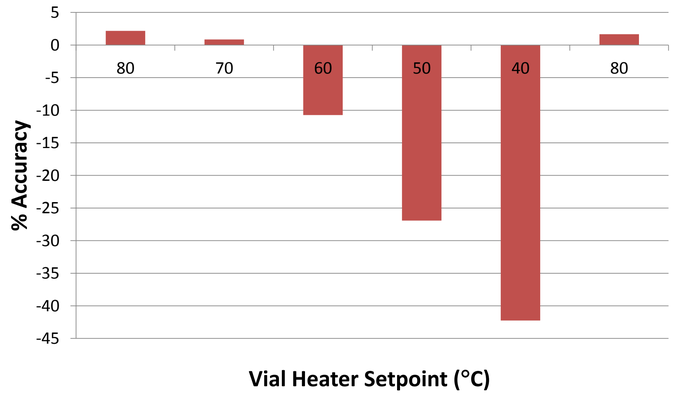

Figure 3. Accuracy of 25 mL aliquots of S200 dispensed

Vial Temperature & Sample Viscosity

Figure 4 shows the rate of sample cooling when 1 mL of a viscosity standard (S200) is moved from the vial heater to the liquid autosampler at 30, 40, 50, 60, 70 and 80 °C vial heater settings. Vertical lines in Figure 4 indicate the time required to move samples from the vial heater to liquid sampler and aspirate the sample at 60 seconds and dispense the sample at 90 seconds. The syringe draw and dispense speeds were set to 40 and 60 µL/min, respectively, with a viscosity delay of 7 seconds and an overfill of 5%. Figure 5 shows the change in viscosity that occurs during cooling corresponding to the vial movement, draw and dispense sequence. Figure 6 shows the cooling rate of a sample placed directly into a vial compared to a micro-waterbath constructed using a 150 µL vial insert submerged in 1.4 mL of water.

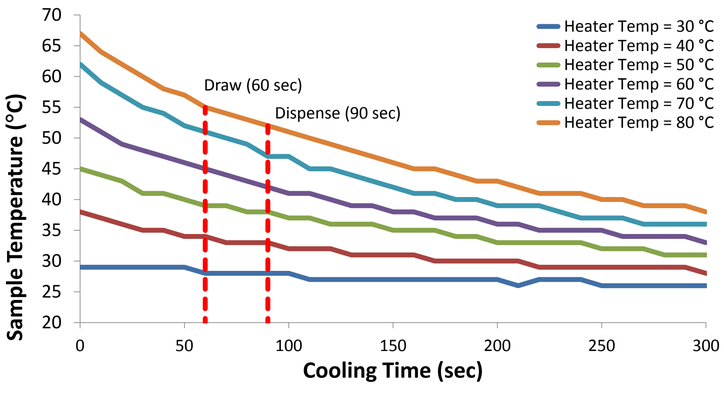

Figure 4. Rate of sample cooling during vial transfer

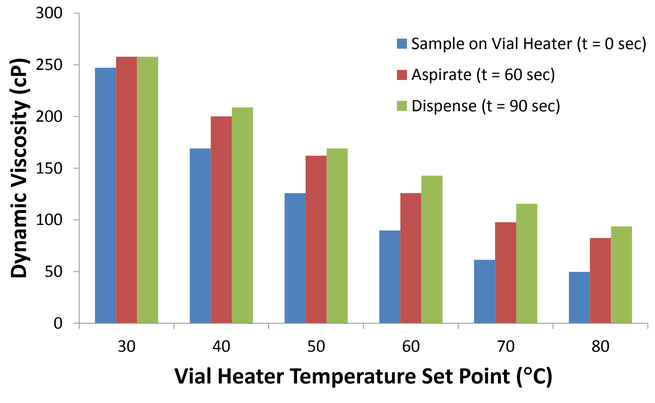

Figure 5. Viscosity changes during vial transfer

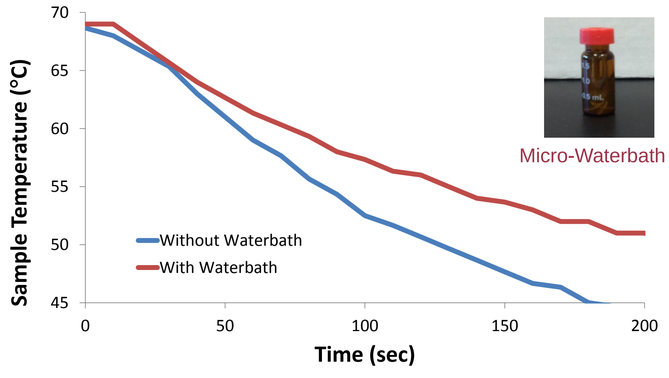

Figure 6. Rate of cooling with and without micro-waterbath

Vacuum Gas Oil Sample Dilution

Table 1 shows the masses and precision of 5 samples prepared by diluting 50 µL using two separate 25 µL aliquots into 950 µL of toluene measured using the WeighStation. Table 2 shows the accuracy and precision of the sulfur and nitrogen determination by GC/XCD.

Table 1. Precision of VGO sample preparation

Sample	Aliquot 1 Mass (g)	Aliquot 2 Mass (g)	Aliquot 1 + 2 Mass (g)
VGO Dilution 1	0.02137	0.02155	0.04292
VGO Dilution 2	0.02232	0.02233	0.04465
VGO Dilution 3	0.02100	0.02096	0.04196
VGO Dilution 4	0.02181	0.02147	0.04328
VGO Dilution 5	0.02215	0.02205	0.04420
Average	0.02173	0.02167	0.04340
Standard Deviation	0.0005	0.0005	0.00106
RSD (%)	2.51	2.46	2.45

Table 2. Accuracy and Precision of VGO sulfur and nitrogen determination

Sample	Sulfur Concentration (ppm)	Nitrogen Concentration (ppm)
VGO Dilution 1	1000	1229
VGO Dilution 2	945	1156
VGO Dilution 3	995	1227
VGO Dilution 4	983	1253
VGO Dilution 5	991	1220
Average	983	1217
Accuracy (% Error)	4.7	3.1
Precision (% RSD)	2.23	3.00

Discussion and Conclusion

Techniques for Viscous Liquid Transfer

In addition to reducing draw and dispense speeds, increasing viscosity delay, and increasing the percent overfill of the syringe; vial heating is an effective means of optimizing the precision and accuracy of viscous liquid transfer due to the large reduction in viscosity with increasing temperature. At room temperature, the S200 standard has a viscosity of 443 cP (centipoise) which drops to 50 cP at 80 °C. The 4-fold increase in temperature results in a 9-fold reduction in viscosity. As illustrated in Figure 1, vial temperature settings between 65 and 80 °C result in the delivery of S200 aliquots within the accuracy tolerance of the 25 mL syringe. When the vial heater temperature drops below 66 °C, the viscosity reaches 109 cP resulting in a significant increase in accuracy and precision errors (Figures 2 and 3). In developing a method, sample cooling occurring during vial transfer from the heater to the autosampler must be considered. Figure 4 shows sample cooling curves at various vial temperature settings with draw and dispense times indicated. The rate of cooling increases with increased temperature settings. As a result, the corresponding change in viscosity increases with increasing vial temperature (Figure 5). Two strategies may be used to minimize the effect of cooling. First, the total volume of sample transferred may be split into multiple aliquots returning the vial to the heater in between aliquots particularly if a slow syringe draw speed is required. A second strategy is to use a micro-waterbath assembly as shows in Figure 6 which becomes more effective at maintaining temperature as cooling time increases.

Vacuum Gas Oil Sample

The strategies investigated for the viscosity standard were applied to a VGO sample. The VGO sample appeared biphasic at room temperature with a significant waxy component. Sample homogeneity occurred around 40 °C. The viscosity was estimated to be 300-400 cP at room temperature. The sample was heated to 80 °C using a micro-waterbath and the 50 µL volume required for the analysis was divided into two 25 µL portions returning the vial to the heater in between aliquots. Table 1 shows the precision of each 25 µL aliquot and the total 50 µL dispensed. Table 2 shows the accuracy and precision of the nitrogen and sulfur determination. The bias in accuracy was attributed to some solvent evaporation as the result of a several day delay between preparation and analysis.

Conclusion

The use of the Sample Prep WorkBench for preparing viscous VGO samples for total sulfur and nitrogen analysis was successfully demonstrated. The techniques developed for this application may be applied to the preparation of other viscous liquids.