Automated Preparation of Simulated Distillation Standards and Samples for ASTM Methods D2887, D7213, D7398 and D6352 using the 7693A System with Easy SamplePrep Software

Application Note

Hydrocarbon Processing

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Abstract

A dual tower Agilent 7693A and tray system installed on the Agilent 7890A GC system is used for the preparation of hydrocarbon calibration standards, solvent blanks, and petroleum samples for analysis by simulated distillation (SimDis). The front tower is equipped with a 5-µL syringe while the back tower is equipped with a 250-µL syringe. A 150 sample tray with heater and mixer/barcode reader is also used. Procedures are described for sample preparation for ASTM D2887, D7213, D7398 and D6352. The Multimode Inlet (MMI), G3510, operated in a temperature programmed split mode is used for all samples. On-line sample preparation programs are constructed using Easy SamplePrep software, an add-on software module for the multitechnique ChemStation.

Introduction

Sample and calibration standard preparation for various simulated distillation methods is normally a manual process requiring dilution, mixing, and heating. Many procedures use volatile toxic solvents such as carbon disulfide. ASTM method D2887 commonly uses CS_2 for sample dilution while D6352 may use CS_2 or toluene for polywax calibration standard preparation. Sample heating, mixing and solvent addition is available with the automation capabilities of the Agilent 7693A tower and tray system. Lab safety is improved by using small quantities of solvents with controlled heating, and mixing in sealed 2-mL vials.

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Experimental

The Agilent 7890A GC system was equipped with two Agilent 7693A towers and 150 sample tray. The front tower used a standard 5-µL or 10-µL syringe and the rear tower was equipped with the optional large syringe carriage with a 250-µL syringe. Sample prep procedures were done by manipulating vials in the sample tray and in the tower turrets. Sample injection occurred on the front tower. The Agilent 7890A was configured with the multimode inlet (MMI) operating in temperature programmed split mode. Detection was with FID. Instrumental parameters for various configurations are listed in Table 1.

Discussion

A number of options or paths to construct sample prep programs using the drag and drop icon implementation of Easy SamplePrep software is possible. This discussion will in general illustrate just one possible solution for each procedure. Screen captures are used to detail the steps and advanced syringe settings.

Table 1. Agilent 7890A GC System SimDis Parameters

System for D2887	
Column	10 m × 0.53 mm, 3.0 µm DB-2887
Oven	40 °C (0 min) to 350 °C (5 min) @ 15 °C/min
Inlet	Multimode (MMI), G3510, 100 °C (0 min) to 340 °C (to end of run) @ 250 °C/min
Liner	Single taper with glass wool, No. 5183-4711
Split	4 to 1
Flow	12 mL/min, constant flow mode
System for D7213 and D7398 (Polywax 500 calibration)	
Column	5 m × 0.53 mm, 0.15 µm DB-HT SimDis
Oven Program	35 °C (0 min) to 400 °C (5 min) @ 10 °C/min
Inlet	Multimode (MMI), 100 °C (0 min) to 400 °C (20 min) @ 250 °C/min
Split ratio	5 to 1
Flow	14 mL/min, constant flow mode
Agilent 7890A GC system for D6352 (Polywax 655 calibration)	
Column	5 m × 0.53 mm, 0.15 µm DB-HT SimDis
Oven Program	35 °C (0 min) to 435 °C (2 min) @ 10 °C/min
Inlet	Multimode (MMI), 100 °C (0 min) to 430 °C (hold to end of run) @ 250 °C/min
Split ratio	5 to 1
Flow	15 mL/min, constant flow mode
Agilent 7693A system	
Front tower	5 µL syringe, G4513A
Back tower	250 µL syringe, G4521A syringe carriage
Tray	150 sample capacity with Heater/Mixer/Bar Code Reader, G4520A
ChemStation	B.04.02 SP1
Sample Prep	G7300AA, Easy SamplePrep
Agilent 7890A GC system firmware	A.01.10.3 or greater
Standards and vials	
Calibration mix, C5-C40, No. 5080-8716	
Calibration mix, C5-C18, No. 5080-8768	
RGO, No. 5060-9086	
PW500, No. 5188-5316	
PW655, No. 5188-5317	
Empty vials with 100 µL inserts, No. 5188-6592	
Simulated Distillation Software	
G2887BA	

Two-milliliter vial resources are assigned in user defined tray locations as shown in Figure 1. These are the resources needed for methods D2887, D7213, D6352, and D7398. The polywax standards are handled differently, usually as "Sample (front)" vials when the front tower is used for injection. Resource vials are specified for use by maximum volume extracted or by number of allowed uses. Ensure that appropriate syringe details such as draw and dispense speeds for the handling of a given chemical resource are set. An example of advanced settings for use of CS_2 is shown in Figure 2.

A typical sample preparation program for D2887 setup (blank, calibration, reference gas oil) may consist of a sequence of three methods, each for a specific sample prep and injection. An example sequence is shown in Figure 3. This illustrates preparation of the blank, calibration standard, and reference gas oil (RGO) samples necessary to set up and verify a system for routine analyses.

The Easy SamplePrep programs used for methods CS2 BLANK, C5C40 CAL 2887, and RGO 2887 are shown in Figures 4, 5, and 6, respectively. Using three methods in a sequence is convenient since each method has different integration parameters.

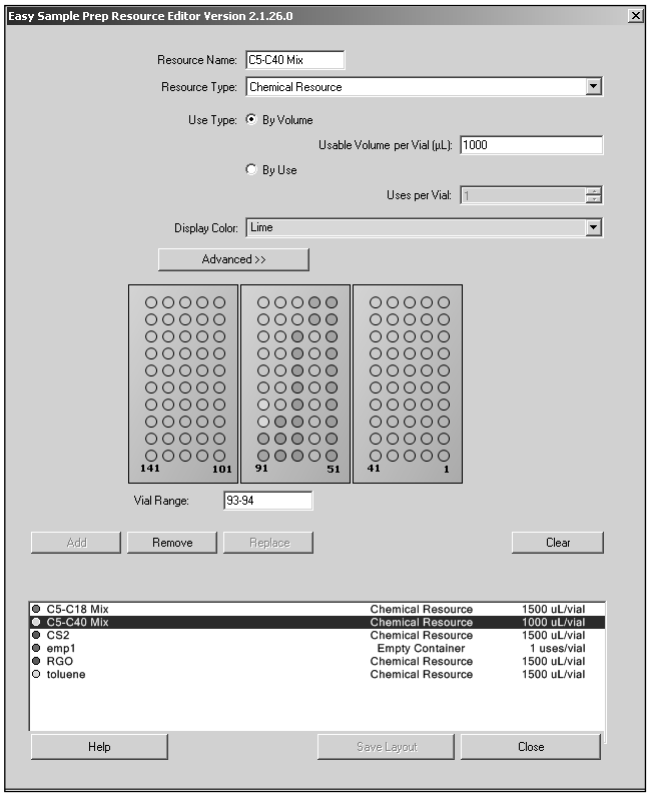

Figure 1. Example resource layout for various simulated distillation procedures. Each resource is assigned a unique color.

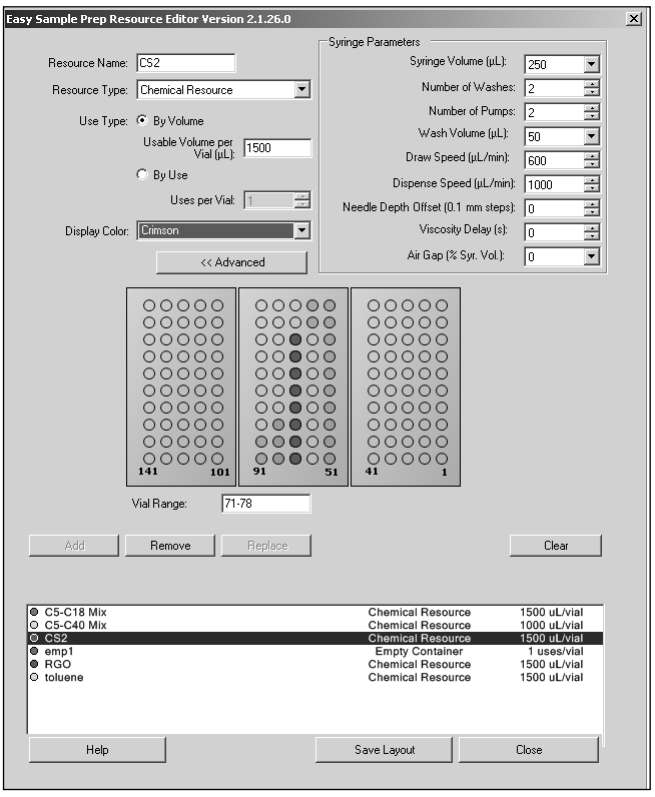

Figure 2. Advanced parameters shown (upper right box) for chemical resource CS2.

Line	Vial	Sample Name	Method Name	Inj/Vial	Sample Type
1	1	blank	CS2 BLANK	2	Sample
2	1	C5-C40	C5C40 CAL 2887	1	Sample
3	1	RGO	RGO 2887	1	Sample

Figure 3. Sequence for setup of D2887. Each method contains the appropriate EasySample Prep procedure.

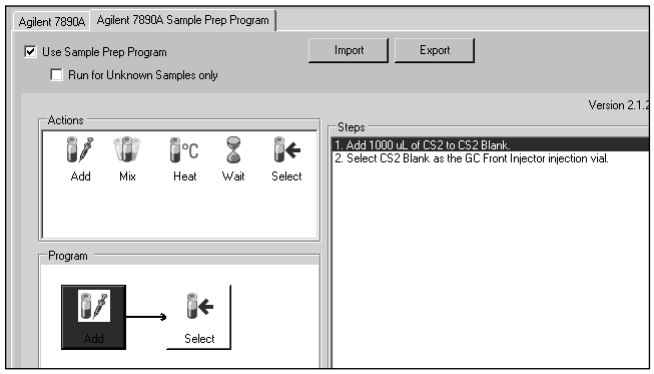

Figure 4. Easy Sample Prep program for the preparation of a CS_2 blank. An empty tray vial has been assigned the name "CS2 Blank". The select icon indicates that the prepared vial is to be injected.

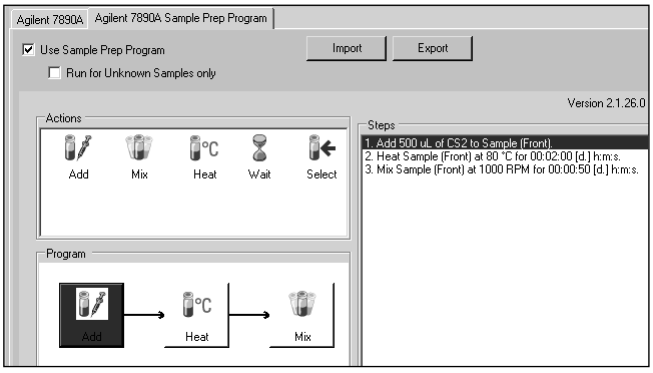

Figure 5. Easy Sample Prep program for preparation and injection of the C5 to C40 calibration mix. The "sample [front]" label defines sequence vials for the front tower.

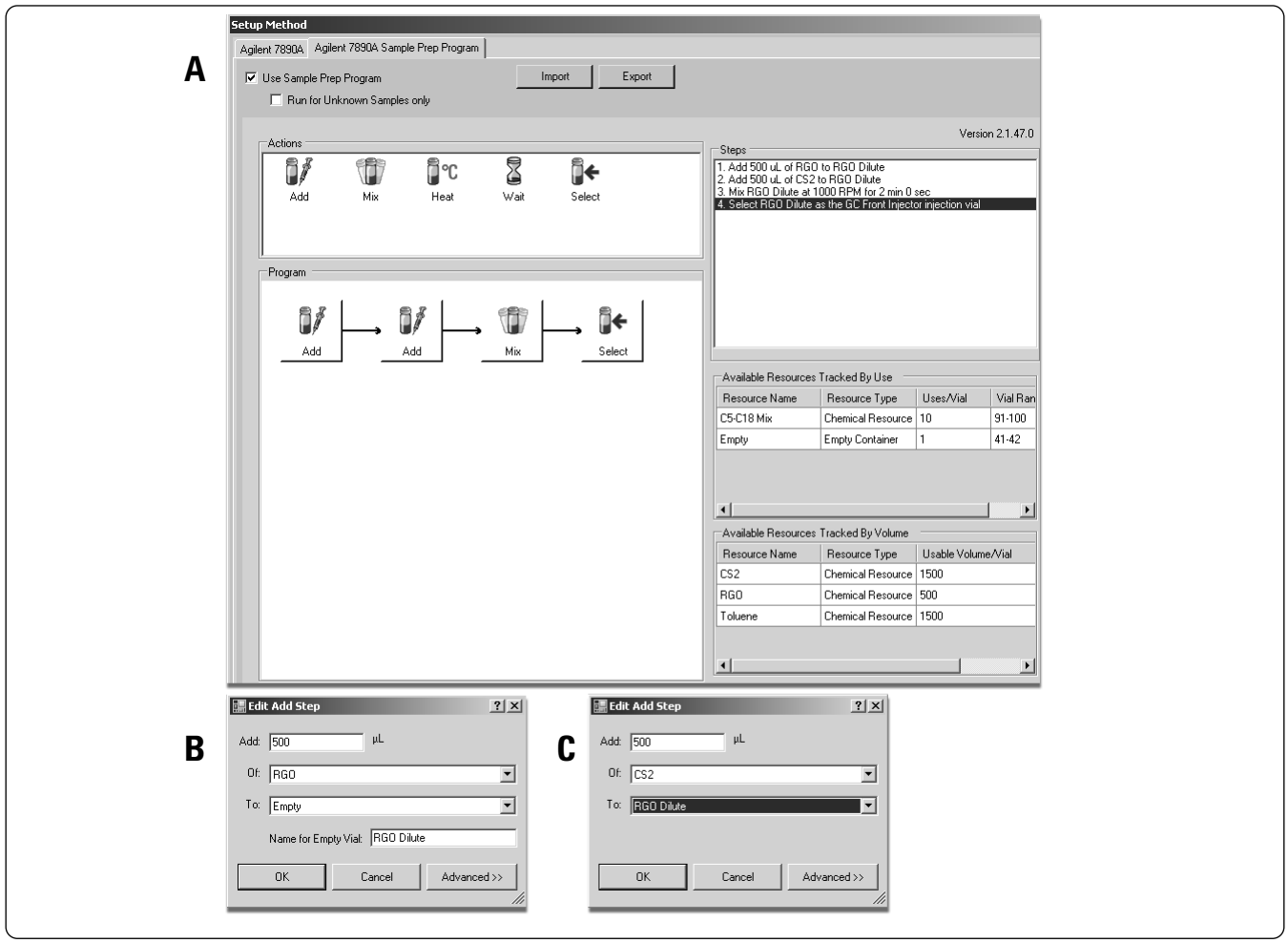

Figure 6a. Easy Sample Prep program for preparation and injection of RGO. An empty tray vial(empty) has been assigned the name "RGO Dilute" during the "Add" step and is selected for injection after prep. "Selected" vials override the vial number given in the sequence table.

Figure 6b. Add steps for RGO and vial naming.

Figure6c. Adding carbon disulfide to the RGO vial.

Upon completion of the sequence, all three prepared vials will have been injected producing data files ready for analysis by simulated distillation software. Note that two blanks are run to ensure both are the same; otherwise, additional blanks should be run. As an alternate setup, the calibration, prepared RGO, and blank vials can be fitted with 100-µL inserts to minimize solvent and resource amounts used for the procedure. Please note that when these inserts are used, limit mixing to speeds of approximately 500 rpm to avoid "spilling" liquid over the top of the insert into the bottom of the 2-mL vial.

Syringe washing is important to incorporate into these programs to avoid contamination or carryover for each vial addition. An example of settings is shown in Figure 7.

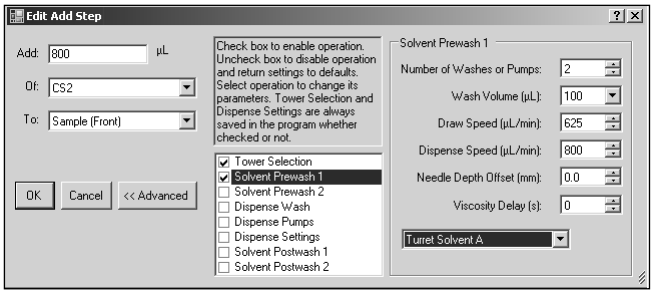

Figure 7. An example using solvent wash vial 1 (5 mL) in the turrent of tower A.

Preparation of polywax standards for the higher temperature SimDis methods can be challenging due to their low solubility. Solvents such as CS_2 and toluene are commonly used. Heating of the solvent/polywax vial is required just prior to injection. This entire procedure can be automated with the Agilent 7693A tower and tray system. The basic procedure for Polywax 655 is as follows:

- Manually place approximately 80 – 100 mg of polywax 500 in a 2 mL vial and seal
- Add 1.5 mL of toluene to the polywax vial
- Add 10 µL of C5-C18 to the polywax-toluene vial
- Mix the vial
- Heat the vial at 80 °C for 4 min.
- Return to tray
- Heat one final time just prior to injection by setting injection/tray parameters in the core ChemStation method

Figure 8 shows the basic prep procedure using a dual tower/tray system automating the steps shown above. The only manual step is adding the solid polywax 500 to Vial 1 (Sample front). This procedure is applicable to D7213 SimDis and D7398 (Boiling Range Distribution of Fatty Acid Methyl Esters).

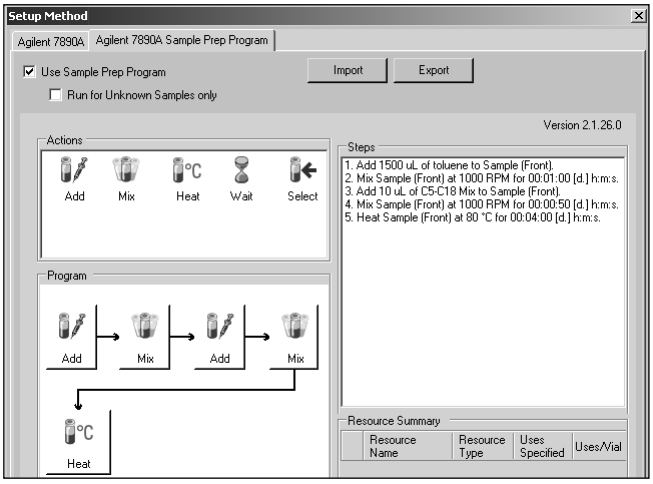

Figure 8. Polywax 500 prep procedure.

A resulting chromatogram for the injection of the prepared PW500 vial (vial 1) is shown in Figure 9. A symmetric distribution of the polyethylene fragments with good resolution to C80 is shown.

The preparation program for Polywax 655 is essentially the same as shown above for PW500 except that heating is extended for 6 minutes typically for dissolution. Prior to injection, the prepared vial is heated for another 3 minutes. Parameters for this second heating step are set under the core ChemStation injection parameter menu item. In the chromatogram shown in Figure 10, a small amount (5 µL) of C_5-C_{18} mix was added to the PW655/toluene solution as part of the automated procedure. This allows calibration starting at C12.

The chromatogram was produced with the multimode inlet set in temperature programmed split mode. Good definition of polyethylene fragments to over C110 are seen in Figure 11. The last 5 minutes of the chromatogram are zoomed to show detail. Producing this detail out to C110 is extremely difficult for any chromatographic system.

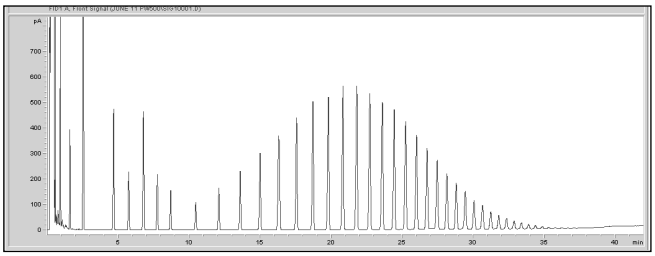

Figure 9. Polywax 500 with C5-C18 added. Multimode inlet, 2.5-µL injection.

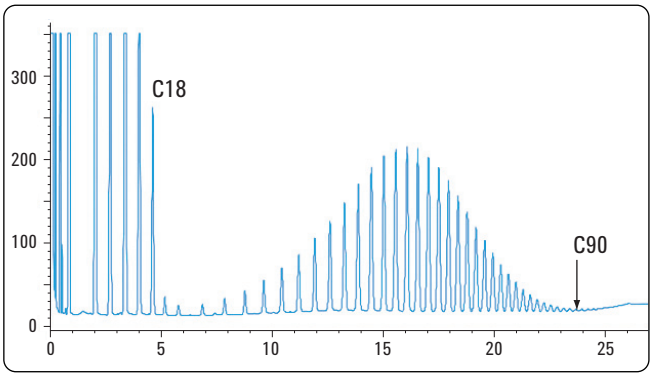

Figure 10. Chromatogram of PW 655.

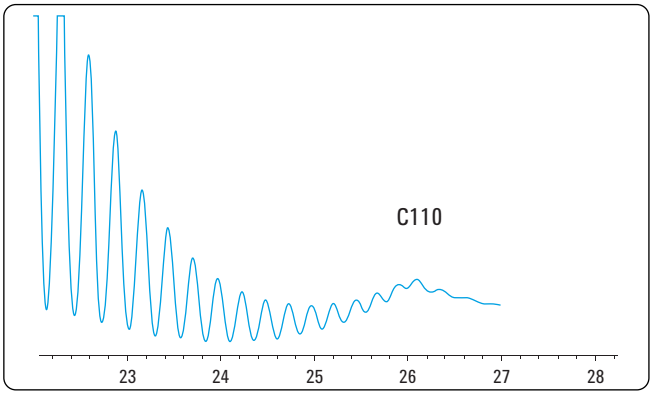

Figure 11. Polywax 655 to C110. Multimode inlet program: 150 °C (0 min) to 430 °C (hold to end of run) @ 200 °C/min. 7890A oven: 40 °C (0 min) to 430 °C (5 min) @ 15 °C/min. 3-µL injection. Solvent is toluene.

Reproducibility of sample preparation steps for the dilution of a heavy vacuum gas oil sample (HVGO) is illustrated in Figure 12. Carbon disulfide was used for sample dilution. Tray vial 1 is the stock HVGO sample, prepared by manually adding 0.5 g of the oil to a 2-mL vial. This material is extremely viscous and cannot be drawn into a syringe without dilution. The program performs a fully automated dilution prior to injection. (Figure 13)

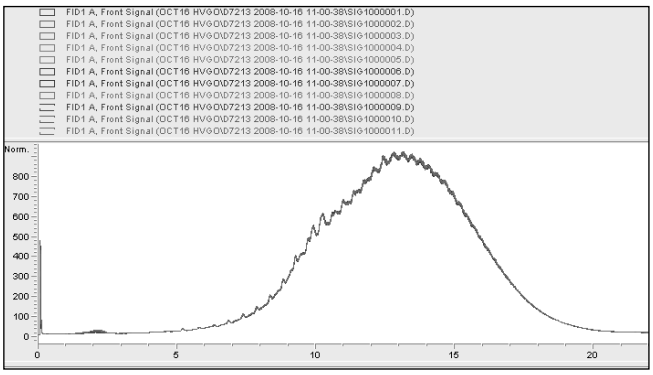

Figure 12. Overlay of 11 runs of HVGO, each prepared by using a Easy Sample Prep program.

Summary

Difficult sample preparation procedures that are commonly used for petroleum and fuel samples can be easily automated on-line with the Agilent 7693A tower and tray system for the Agilent 7890A GC system and Agilent 6890N Network GC system, including A, and Plus models using the Easy SamplePrep add-on software for the multitechnique ChemStation. The system is particularly well suited for preparation of polywax calibration samples used for higher temperature methods. Tasks such as mixing, solid dissolution, dilution, heating, viscosity reduction, and internal standard addition are easily accomplished by assembling icon based instructions. User contact with toxic solvents such as CS_2 is greatly reduced. The software monitors used resources and moves to the next available resource vial as assigned in the resource table when needed.

Chromatographic performance is enhanced through use of the multimode inlet. Using standard split injection liners, good sample capacity without carryover and with minimal discrimination of wide boiling samples is achieved. The inlet was used in the temperature programmed split mode for this work. Cryo cooling was not used, however, carbon dioxide cryo can be used optionally to shorten inlet cool down if desired.

The sample prep procedures listed here represent just one way of accomplishing a given task. Using the icon based commands available with the system, there are many variants that lead to the same end result.

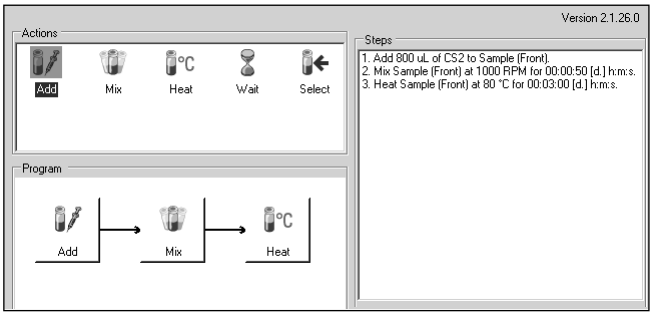

Figure 13. Preparation of HVGO for injection. CS_2 is used as the solvent.

Reference

1. Roger L. Firor, “Automated Preparation of Simulated Distillation Samples for ASTM Methods D2887, D7213, D7398, and D6352 using a Dual Tower 7693A and Tray System”, April 2009, Agilent Technologies publication 5990-3778EN.

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