

This application note describes the steps involved in using the FROG 5000 for the analysis of Gasoline Range Organics.

Preparing Standards for Gasoline

Since gasoline is soluble in methanol, all gasoline standards can be prepared in methanol.

For example, to prepare a 500 µg/mL Gasoline solution in methanol, make a 10mL solution containing 7 µL gasoline.

$$\text{Volume of Gasoline} = \frac{\text{Concentration of Final Solution} \left(\frac{\mu\text{g}}{\text{mL}} \right) * \text{Volume of Final Solution (mL)}}{\text{Density of Gasoline} \left(\frac{\text{g}}{\text{mL}} \right) * 10^6 \left(\frac{\mu\text{g}}{\text{g}} \right)} * \frac{10^3 \mu\text{L}}{\text{mL}}$$

$$= \frac{500 \frac{\mu\text{g}}{\text{mL}} * 10 \text{ mL}}{0.711 \frac{\text{g}}{\text{mL}} * \frac{10^6 \mu\text{g}}{\text{g}}} * \frac{10^3 \mu\text{L}}{\text{mL}} = 7 \mu\text{L Gasoline}$$

Preparing Samples for Calibration

Since the FROG analyzes 5mL water samples, a calculation must be performed to determine proper preparation of the desired concentration of gasoline. For example, to prepare a 100 ppb gasoline sample, inject 1 µL of 500 ppm (µg/ml) gasoline standard into 5 mL of water. This sample can then be analyzed with the FROG. To run a calibration for gasoline range organics, it is recommended that one run a series of samples, working from low concentration to high concentration. For a linear calibration, a minimum of 3 samples should be run.

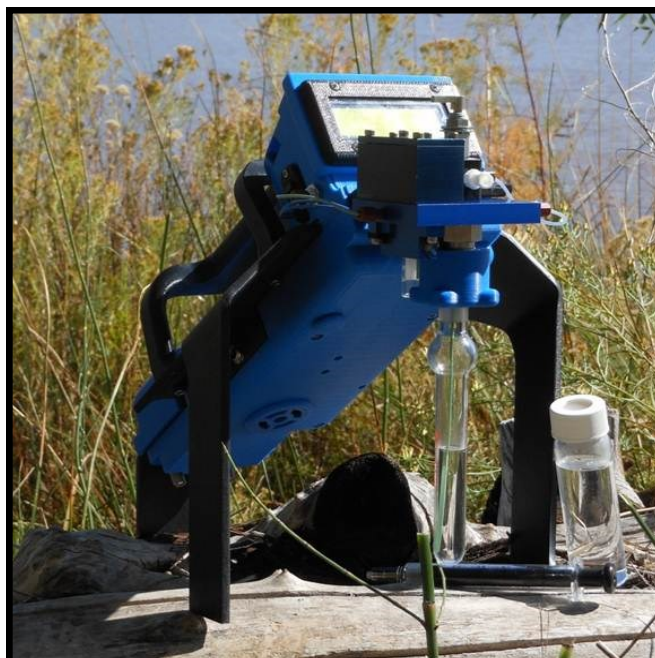
$$M_1 V_1 = M_2 V_2 \rightarrow V_1 = \frac{M_2 V_2}{M_1} = \frac{100 \text{ ppb} * 5 \text{ mL}}{500 \text{ ppm} * 10^3 \text{ ppb/ppm}} * \frac{10^3 \mu\text{L}}{\text{mL}}$$

$$= 1 \mu\text{L of 500ppm Gasoline Standard}$$

Instrument Settings

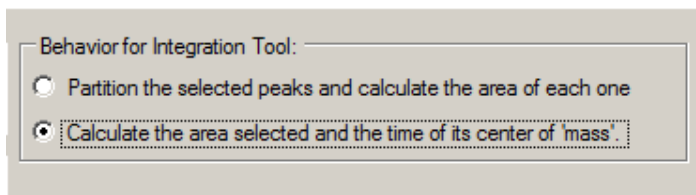
T _a	420
T _b	90
T _c	180
C _t	40
H _t	130
Collect	45
Clean	4
Presettle	4
Settle	2
Fire	6

These FROG instrument settings are recommended for the analysis of GRO. Note that the Ct setting of 40°C is only possible if using in a cool environment. If the FROG is being used outdoors in a hot climate it is recommended that Ct be set to 5°C hotter than the ambient temperature.



Integration of Total Gasoline Range Organics

Integration of all peaks should be enabled in order to determine the total concentration of GRO. To enable this type of integration, a different behavior for the integration tool should be selected. To do this, go to the Settings tab in Ellvin Software, find "Behavior for Integration Tool" and select "Calculate the area selected and the time of its center of 'mass'." This will allow for integration of the total VOCs present in the sample.



To Integrate, first open the desired data file in Analyze tab and then under "Operations" select "Flatten Beta."

Figures 1 and 2 show how "Flatten Beta" smooths and flattens the baseline for easier integration.

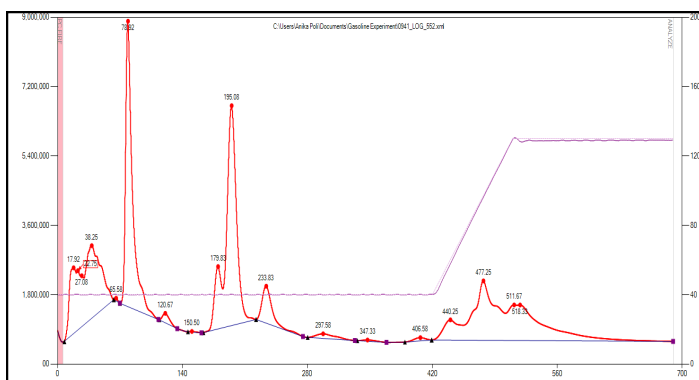
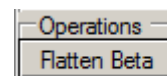


Figure 1: Gasoline chromatograph in default mode

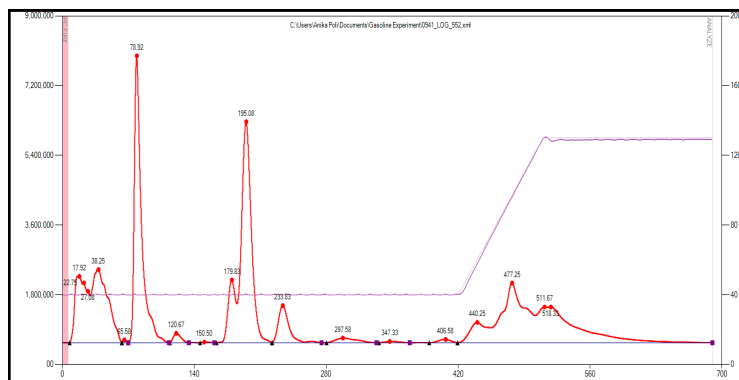


Figure 2: Gasoline chromatograph after using "Flatten Beta"

With a flattened baseline integration is quite simple. The use of integration tool 2 is recommended. To use the integration tool, one should select the point at the beginning of the chromatograph along the baseline and drag to a point on the baseline at the end of the chromatograph, see figure 3. This integration includes the area underneath all the peaks.

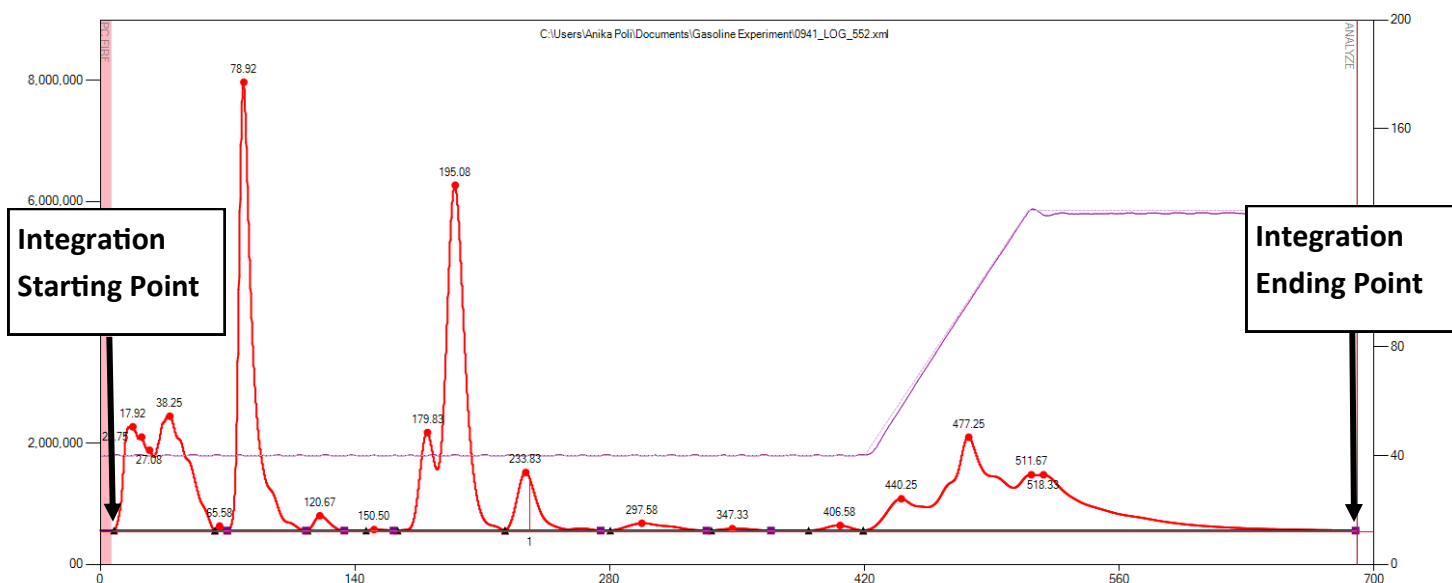


Figure 3: Integration of gasoline chromatograph. Notice that the entire chromatograph is integrated as one area under the curve.

Once the chromatogram is integrated, the data can be added to a calibration. Using the GRO integration technique allows a user to set up a calibration for GRO rather than individual compounds present in gasoline. However, gasoline samples can be analyzed and integrated to determine the concentrations of individual chemicals including those in BTEX. The locations of the BTEX chemicals are shown in figure 4.

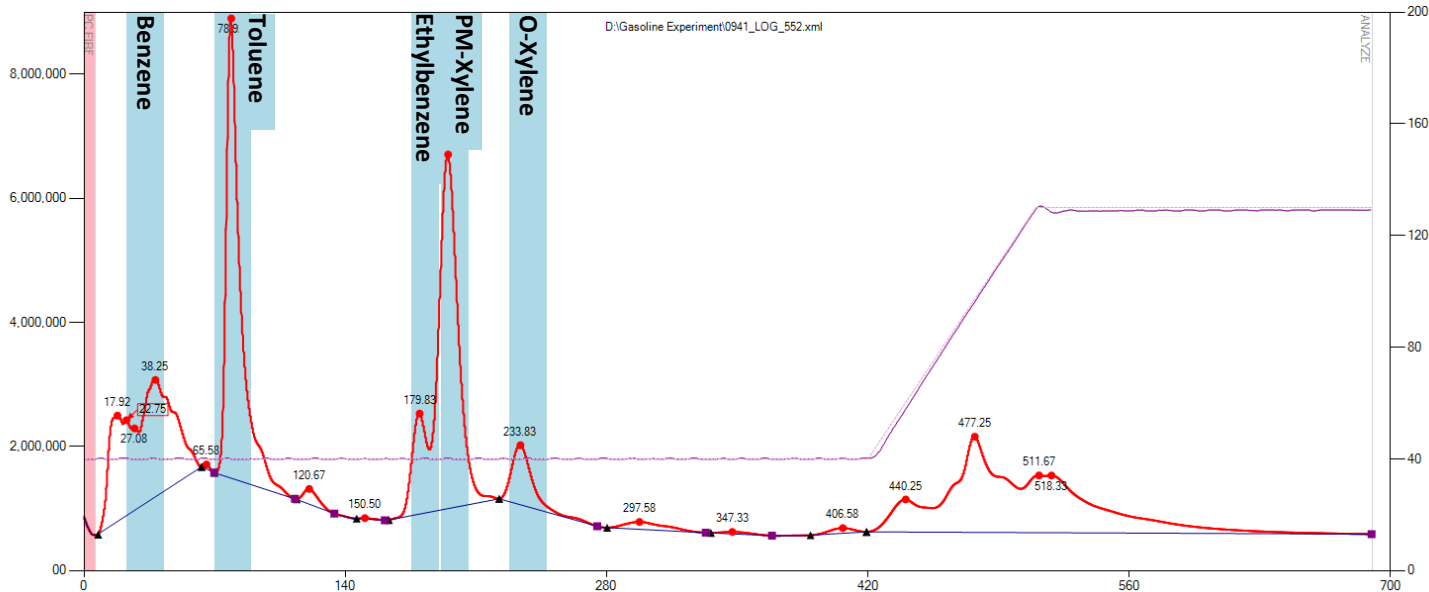
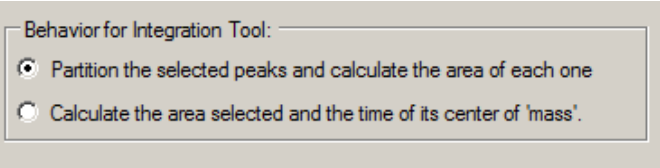


Figure 4: BTEX peaks present in a gasoline sample

To integrate a gasoline chromatogram for BTEX, the behavior for the integration tool should be set to “Partition the selected peaks and calculate the area of each one.” Then one can integrate normally as outlined in the FROG-5000 quick start guide and user’s manual. Note that if analyzing samples for BTEX a separate BTEX calibration should be completed. A GRO calibration alone does not have enough information to determine BTEX calibrations. This is because different gasoline standards may contain different amounts of BTEX.



Summary

With the right settings and integration techniques the FROG– 5000 can be calibrated for the analysis of gasoline range organics. The FROG-5000 also excels at analyzing gasoline samples for BTEX using basic integration techniques. For more information about using the FROG-5000 for analysis of gasoline call us at 505-999-5880 or email at info@defiant-tech.com.



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Can the FROG-5000 be Used to Analyze Diesel?

The FROG-5000 is not recommended for analysis of diesel. First there is the issue of solubility, diesel is not soluble in methanol which is the solvent of choice for preparing standards to be used with the Frog. If one attempts to use the FROG-5000 for the analysis of diesel range organics, some chemicals will appear as peaks on the chromatograph, but the results will be inconsistent. This inconsistency is best explained by the inefficiency of sparging of diesel samples. If a calibration is attempted one will find that there is no correlation between peak area and concentration.