RESTEK

environmental

Applicationsnote

UST Monitoring: Fast Sample Turn-Around, Using Rapid Temperature Programming

Widespread use of underground tanks to contain all types of fuels and lubricants dictates that environmental laboratories perform frequent UST (underground storage tank) analyses according to state or federally mandated guidelines. Tests are required during site assessments, to determine whether releases have occurred, and after closure of a site, to ensure it is safe for alternate uses in the future. Toxicity of hydrocarbons has been documented as both acute and chronic, so it is important for site managers to monitor surrounding streams, wastewater, and soils for possible migration of these fuels. Laboratory verification of results from on-site quick tests can present a large number of samples and a need for immediate results.

With so many analyses, testing laboratories would benefit from shorter run times that would make sample turn-around faster. Fast temperature programs can speed up elution of high boiling point compounds and late eluters, but often are not used to maximum advantage. The Agilent 5890 has a maximum temperature program rate of 70°C/min., but the factory heating elements in the 5890 only allow this maximum rate to be maintained up to a temperature of 100°C. The Agilent 6890 allows a maximum ramp rate of 75°C/min. at starting temperatures of 50–70°C and 20°C/min. at starting temperatures of 300–450°C.* For analysts trying to push temperature ramps as fast as possible, these restricted program rates can lead to longer analysis time and broader peaks.

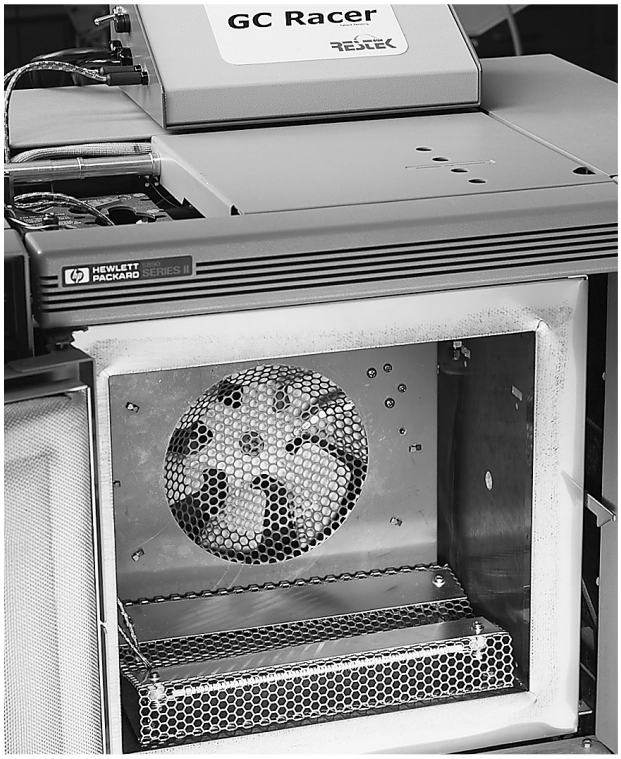
The GC Racer temperature programming system** enhances conventional ovens with an auxiliary heater that is controlled by the GC. The GC Racer system will maintain a temperature program rate of 70°C/min. up to 350°C or 60°C/min. to temperatures as high as 450°C in an Agilent 5890 or a rate of 70°C/min. up to 400°C in an Agilent 6890. The GC Racer consists of a control unit and a resistive heating element that is placed on the floor of the GC oven (Figure 1). The heating element is connected to the controller, which is plugged into the main PC board of the GC and into a 120V standard grounded wall outlet. When the GC Racer controller detects that the factory heating elements are not keeping up with the programmed heating rate, the GC Racer heater is brought into the circuit to augment the heat being supplied to the oven. The auxiliary heater design is similar to that of the original GC heater. At no time during the installation of the GC Racer system is the column removed from the oven, or disconnected from the detector or injection port.

Example application: TNRCC

TNRCC Method 1005, Revision 03 - the current UST method released by the Texas Natural Resource Conservation Commission in June 2001 - describes liquid/liquid sample preparation for aqueous and solid samples, followed by capillary GC-FID analysis. Samples must be analyzed for hydrocarbons in two boiling point / carbon number ranges: C6-12 and C12-C28, and in an optional C28-C35 range if presence of heavier fuels or lubricating oils is suspected. Method 1005 can be used in conjunction with a second (draft) method, TNRCC Method 1006. In this method, authorized in 2000, solid phase extraction on silica gel is used to separate the total petroleum hydrocarbons (TPH) extract obtained in Method 1005 into aliphatic and aromatic fractions, to further characterize and define the initial samples.

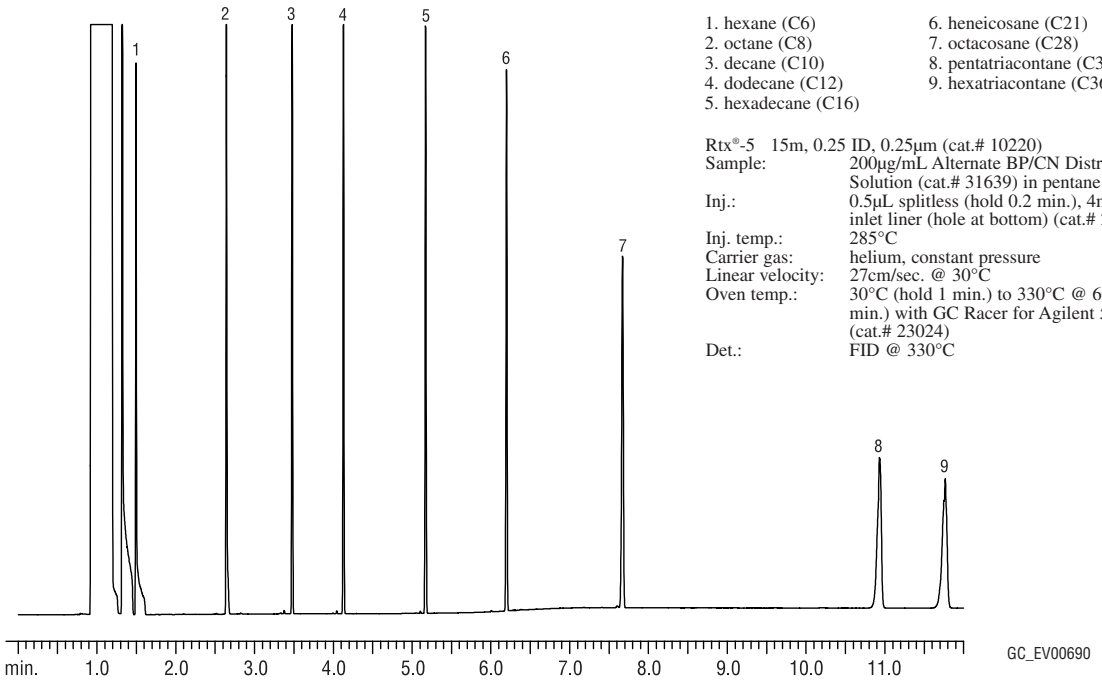
Analysis techniques for both TNRCC methods are complex, and several analytical reference mixes are used to ensure that the analytical system meets the basic quality criteria set in the methods. The column and GC conditions must be optimized so that the solvent peak is well separated from the C6 peak, for adequate quantification of volatiles in the samples. It is also important to minimize injection port discrimination, so that heavy range hydrocarbons can be properly quantified: the C35 response must be greater than 75% of the C28 response. *n*-Alkane markers are used to define approximate boiling point / carbon number distribution ranges for calibration and reporting purposes. Finally, matrix spike solutions containing diesel fuel and unleaded gasoline composites, and surrogates, are used as "real world"

Figure 1 - GC Racer temperature programming system installed in an Agilent GC.



**Use of higher voltage and amperage or a special insert purchased with the GC will allow slightly higher ramp rates.*
***Manufactured by Zip Scientific, available from Restek.*

Figure 2 - Texas UST: 12-minute analysis for alternate boiling point/carbon number distribution marker



1. hexane (C6)
2. octane (C8)
3. decane (C10)
4. dodecane (C12)
5. hexadecane (C16)
6. heneicosane (C21)
7. octacosane (C28)
8. pentatriacontane (C35)
9. hexatriacontane (C36)

Rtx®-5 15m, 0.25 ID, 0.25µm (cat.# 10220)
Sample: 200µg/mL Alternate BP/CN Distribution Marker Stock Solution (cat.# 31639) in pentane
Inj.: 0.5µL splitless (hold 0.2 min.), 4mm Drilled Uniliner® inlet liner (hole at bottom) (cat.# 20756)
Inj. temp.: 285°C
Carrier gas: helium, constant pressure
Linear velocity: 27cm/sec. @ 30°C
Oven temp.: 30°C (hold 1 min.) to 330°C @ 60°C/min. (hold 6 min.) with GC Racer for Agilent 5890 Series II GC (cat.# 23024)
Det.: FID @ 330°C

check samples, to verify sample preparation techniques and appropriateness of analytical conditions. Analysis times for these standards will be between 20 min. and 90 min., according to the guidelines in TNRCC 1006. After system qualification, each extracted sample is screened for TPH content, as required in TNRCC 1005, and then possibly also for the aliphatic and aromatic fractions, as described in TNRCC 1006.

Checking QA/QC, locator, and calibration mixes can be analyzed rapidly - often in less than 12 minutes - using a GC Racer system installed in an Agilent 5890 or 6890 GC. A temperature ramp rate of 60°C/min. to 330°C during the GC analysis produces quick identification of hydrocarbons across the entire monitored range, from C6 to C35. Figure 2 shows the chromatogram obtained by using a GC Racer and a 60°C/min. temperature ramp for the Alternate Boiling Point/Carbon Number Distribution Marker Stock Standard (Restek cat.# 31639): even when the analysis is extended to C36, analysis time is cut in half, with no loss of resolution, relative to conventional temperature programs.

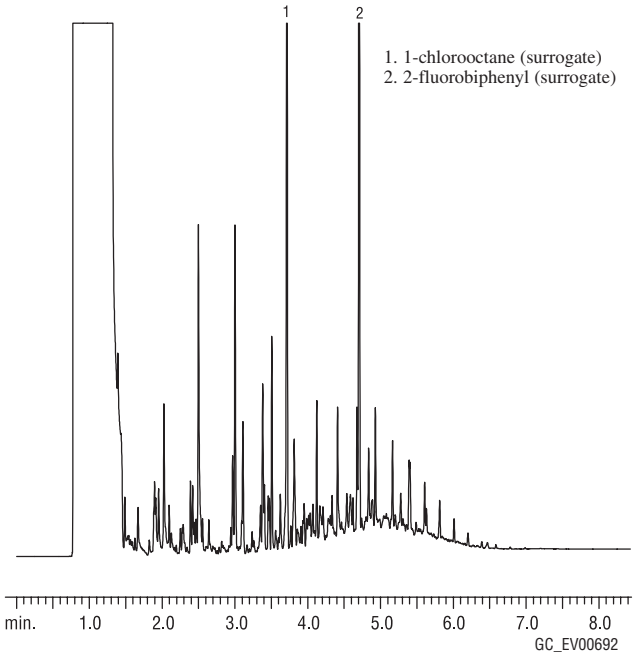
Figure 3 demonstrates the fast identification that is possible for the diesel fuel #2 composite / unleaded gas composite (TX TPH Matrix Spike Mix, cat.# 31484) with surrogate standards (2-fluorobiphenyl, cat.# 31096; 1-chlorooctane, cat.# 30084), as required in methods 1005 and 1006, using the same conditions as in Figure 2. The thin film Rtx®-5 column used in these analyses demonstrates great stability, even at a temperature ramp rate of 60°C/min., and exhibits very low bleed over the entire temperature range, to 330°C.

Example application: Florida DEP

In November 1995, in an effort to develop more environmentally sensitive testing methods, the Florida Department of Environmental Protection (DEP), Division of Waste Management, released the Florida Residual Petroleum Organic

Figure 3 - Texas UST: identify diesel/gas composites in less than 10 minutes

Rtx®-5 15m, 0.25mm ID, 0.25µm (cat.# 10220)
Sample: 1000µg/mL unleaded gas and diesel fuel #2 composites standard (cat.# 31483) in pentane
250µg/mL 2-fluorobiphenyl standard (cat.# 31096) in dichloromethane
250µg/mL 1-chlorooctane (cat.# 30084) in P&T methanol
Inj.: 0.5µL splitless (hold 0.2 min.), 4mm drilled Uniliner® inlet liner(hole at bottom) (cat.# 20756)
Inj. temp.: 285°C
Carrier gas: helium, constant pressure
Linear velocity: 27cm/sec. @ 30°C
Oven temp.: 30°C (hold 1 min.) to 330°C @ 60°C/min. (hold 6 min.) with GC Racer for Agilent 5890 Series II GC (cat.# 23024)
Det.: FID @ 330°C



1. 1-chlorooctane (surrogate)
2. 2-fluorobiphenyl (surrogate)

Method (FL-PRO), Version 1. The FL-PRO method replaces Freon® fluorocarbon extraction with a methylene chloride liquid/liquid extraction and silica gel clean-up for water and soil samples, and recommends analysis by capillary GC/FID.

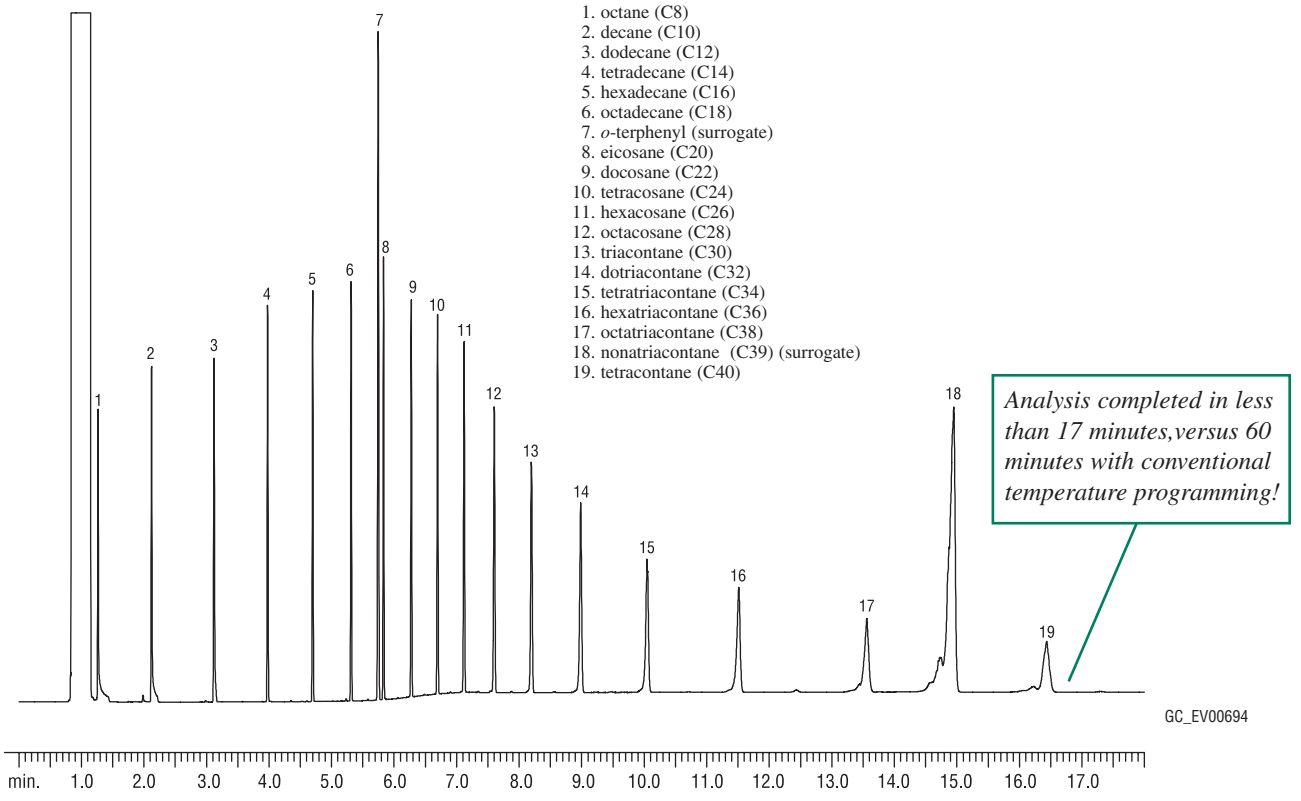
According to the FL-PRO method, samples must be analyzed for alkanes over a range of C8 to C40, which encompasses gasoline, diesel fuel, and motor oil components. The column and GC conditions must be optimized to ensure that the solvent peak is well separated from the C8 hydrocarbon, for reproducibly quantifying the volatile components in the samples. It also is important to assure adequate resolution of the surrogates from the closely eluting alkanes. The technique recommended in the method ensures that the analytical system is able to meet the basic quality criteria set out in the method, but the analytical runs last approximately 60 minutes.

Checking QA/QC, locator, and calibration mixes can be analyzed rapidly - often in less than 17 minutes - using a GC Racer temperature programming system installed in an Agilent 5890 or 6890 GC. A temperature ramp rate of 60°C/min. to 330°C allows quick identification of hydrocarbons across the entire monitored range, from C8 to C40. Figure 4 shows the results obtained by using a GC Racer and a 60°C/min. temperature ramp for the Florida TRPH Standard (Restek cat.# 31266): analysis time is cut by more than two thirds, relative to conventional temperature programs, with no loss of resolution.

A Drilled Uniliner® inlet liner, listed in the conditions for these chromatograms, prevents discrimination against the high molecular weight hydrocarbons, and excellent results can be achieved without the expensive electronic pressure control (EPC) technology option mentioned in the TNRCC method. The hole at the bottom (inlet end) of the liner ensures a sharper solvent peak, with little tailing - ideal for separating and quantifying the volatile C6 or C8 hydrocarbon, which elutes in proximity to the solvent in Figure 2 and Figure 4, respectively. This liner also is compatible with an EPC system, making it a versatile choice and better alternative to standard split/splitless inlet liners.

The simplicity of its components and ease of installation make the GC Racer system a valuable tool in the quest for high-speed GC, and a must-have add-on accessory for every 5890 or 6890 GC. The speed of analysis that can be achieved will lead to direct savings of time and money by decreasing run time and increasing sample throughput.

Figure 4 - Florida UST: rapid analysis for total recoverable petroleum hydrocarbons (TRPH), using a GC Racer and an Rtx®-5 column



Rtx®-5 15m, 0.25mm ID, 0.25µm (cat.# 10220)
Sample: 250µg/mL Florida TRPH standard (cat.# 31266) in hexane, 1,000µg/mL *o*-terphenyl (cat.# 31097) in dichloromethane, 600µg/mL nonatriacotane (cat.# 31456) in carbon disulfide
Inj.: 0.5µL splitless (hold 0.2 min.), 4mm drilled Uniliner® inlet liner (hole at bottom) (cat.# 20756)
Inj. temp.: 260°C
Carrier gas: helium, constant pressure
Linear velocity: 30cm/sec. @ 100°C
Oven temp.: 100°C (hold 1 min.) to 250°C @ 40°C/min. to 330°C @ 60°C/min. (hold 12 min.)
Det.: FID @ 330°C

GC Racer by Zip Scientific

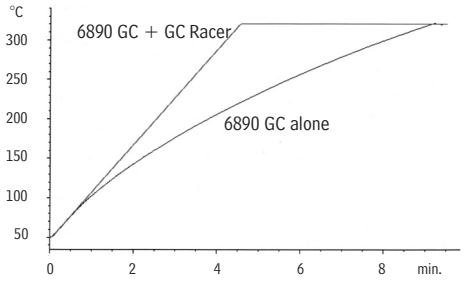
- Saves time and money by increasing throughput.
- Makes fast GC possible with any capillary GC column.
- Easy to operate and install—truly a "plug and use" accessory.

Restek and Zip Scientific have teamed up to bring you the GC Racer temperature programmer, a system that enhances conventional ovens with an auxiliary heater that is controlled by the GC. The GC Racer consists of a control unit and a resistive heating element that is placed on the floor of the GC oven. The heating element is connected to the controller, which is plugged into the main PC board of the GC and into a 120V standard grounded wall outlet. When the GC Racer controller detects that the factory heating elements are not keeping up with the programmed heating rate, the GC Racer heater is brought into the circuit to augment the heat being supplied to the oven.

The GC Racer system will maintain a temperature program rate of 70°C/min. up to 350°C or 60°C/min. to temperatures as high as 450°C in an Agilent 5890 or a rate of 70°C/min. up to 400°C in an Agilent 6890.

The simplicity of its components and installation make the Zip Scientific GC Racer system a valuable tool in the quest for high-speed GC, and a must-have add-on accessory for every 5890 or 6890 GC. The speed of analysis that can be achieved and the ease of installation will lead to direct savings of time and money by decreasing run time and increasing sample throughput.

Figure 5-Faster temperature programs increase sample throughput.



GC: Agilent 6890; Start Temp: 50°C,
Program: 60°C/min. to 320°C

From the Customer....

"We tried a GC Racer Temperature Programmer from Restek and now we want more! With the GC Racer, we can perform high speed temperature programming to get the results we need, and we can use conventional columns and fittings. This is a great time and cost savings for us. Not only that, but, with this system, we don't experience any leaks at the fittings, so we can use it with our mass spectrometer. All this for an economical price."

Josh Hildabrand, Chemist, and William Mock, Lab Manager, Environmental Science Corporation

In a Washington Lab Report, *Environmental Science Corporation was listed 5th in productivity, 2nd in sales for a single-location laboratory, and 13th in overall sales. Keep up the good work!*

Rtx® - 5 Column (fused silica)

(Crossbond® 5% diphenyl/95% dimethyl polysiloxane)

ID	df (µm)	temp. limits	15-Meter
0.25mm	0.25	-60 to 330/350°C	10220

GC Racer* by Zip Scientific

Description	voltage	qty.	cat.#
GC Racer for Agilent 5890 Series II (only) GC	120 volt	ea.	23024
GC Racer for Agilent 5890A (only) GC	120 volt	ea.	23025
GC Racer for Agilent 6890 (only) GC	120 volt	ea.	23028

**Patent pending.*

For analytical reference materials request our Texas UST Fast Facts, lit. cat.# 59394 and/or our Florida UST Fast Facts, lit. cat.# 59395.

For Drilled Uniliner® inlet liners, refer to our current catalog, request our Drilled Uniliner® Fast Facts (lit. cat.# 59877), or visit our web site.

Restek Trademarks: Crossbond, Rtx, Uniliner, Restek logo.
Other Trademarks: Freon (E. I. du Pont de Nemours & Co., Inc.)