

---

# Stability of GC/FTIR instrumentation for the analyses of reformulated gasolines

V. J. Giarrocco and W. P. Duncan  
Hewlett-Packard Co.

## IRD Application Note

**HP 5965B**

**IRD 93-1**

---

### IRD productivity profile

#### Industry

Petrochemical

#### Chemicals

Ethers

Alcohols

Aromatic hydrocarbons

#### Sample matrix

Reformulated gasolines

#### Analysis

Selected wavelength  
quantitation

### Introduction

GC/FTIR has been demonstrated to be a good tool for the analysis of ethers, alcohols, and aromatics in reformulated gasolines.<sup>1</sup> The calibration procedures are labor intensive, however, and require many pure and expensive compounds. It was thought that if the HP GC/IRD were sufficiently stable, the system could be precalibrated at a central laboratory and shipped to field locations as needed. A number of experiments were devised in a cooperative effort between Hewlett-Packard and a major petroleum corporation to determine this stability, and the results are described in the following text.

### Experimental

A Hewlett-Packard 5890 Series II GC/5965B IRD system was configured as follows:

*Column:* J&W 60 m × .32 mm  
5.0 micron DB-1

*Carrier:* H<sub>2</sub> 42 cm/s (20 psi) set  
at 300°C.

*Injector (EPC, electronic pressure control):* On-column with injector heater turned off. A 0.5 m section of 0.53 mm deactivated fused silica tubing was connected between the injector and the column with a Swagelok SS low dead volume union to allow use of an HP 7673B autosampler. The EPC inlet was operated in constant pressure mode.

*Injection volume:* 0.1 microliters with a 5.0 microliter syringe and a nanoliter adapter.

*Oven temperature program:*  
50°C (0 min.)  
2°C/min. to 100°C (0 min.)  
4°C/min. to 140°C (0 min.)  
30°C/min. to 300°C (1 min.).

### IRD parameters

*Light pipe temperature:* 250°C.

*Transfer line temperature:* 250°C.

*Resolution:* 8 cm<sup>-1</sup>

*Scan Rate:* 6 interferograms co-added for one spectrum/second.

*Selective absorbance*

*reconstructions:* Second difference. Function width = 75.

Before each stability test, the following procedure was performed:

1. N<sub>2</sub> purge of the spectrometer at 30 psi was started. There were no restrictors in the N<sub>2</sub> purge lines.
2. The infrared source was allowed to come to full power and equilibrate for 60 minutes. The light pipe and the transfer lines were also brought to operating temperature during this time.
3. The mirror velocity was calibrated.
4. The laser was calibrated with water vapor.

5. The mirror velocity was recalibrated.

6. The spectrometer was purged with N<sub>2</sub> at 30 psi for 4 hours to remove any residual water vapor.

Samples containing twelve oxygenates and five aromatics were used for the stability testing with 1,2-dimethoxyethane (DME) added as an internal standard (ISTD). These compounds along with their respective reconstruction frequencies are listed in Table 1.

**Table 1. Analyte reconstruction frequencies**

Compound	Frequency Range (cm <sup>-1</sup> )
methanol	1055-1063
ethanol	1052-1060
2-propanol	1141-1149
t-butanol	1207-1215
1-propanol	1056-1064
MTBE	1205-1213
2-butanol	1128-1136
DIPE	1122-1130
i-butanol	1037-1045
ETBE	1199-1207
DME (ISTD)	1123-1131
1-butanol	3665-3673
benzene	670-678
TAME	1185-1193
toluene	724-732
ethylbenzene	694-702
m-xylene	763-771
p-xylene	790-798
o-xylene	736-744

Pure compounds were purchased from Aldrich Chemical Co. Eight oxygenate calibration solutions were prepared in toluene by pipetting 1, 2, 3, 4, 5, 10, 15, and 20 ml aliquots of each analyte and 10 ml of DME into respective 100.0 ml volumetric flasks while recording the weights. This bracketed the calibration in the 0 to 20 volume % range. All calibrations were based on weight/weight. Oxygenate test solutions were prepared in gasoline.

Ten aromatic calibration solutions were prepared in n-pentane. 0.5 ml aliquots of benzene from 0.5 to 5 ml, 1, 2, 3, 4, 5, 7, 10, 15, 20, and 25 ml aliquots of toluene, and 1, 2, 3, 4, 5, 7, 10, 13, 15, and 20 ml aliquots each of ethylbenzene, m-xylene, p-xylene, and o-xylene along with 10.0 ml of DME were added to respective 100.0 ml volumetric flasks while recording the weight of each aliquot. These calibrations were based on weight/weight. Aromatic test solutions were prepared in n-pentane.

## Results and discussion

Figure 1 shows a selected wavelength chromatogram (SWC) of the oxygenate analytes and ISTD in gasoline at the level of 1 volume %. Figure 2 shows the Gram Schmidt chromatogram of gasoline, an SWC specific for MTBE and an SWC specific for the aromatic analytes. Following integration of the SWCs,

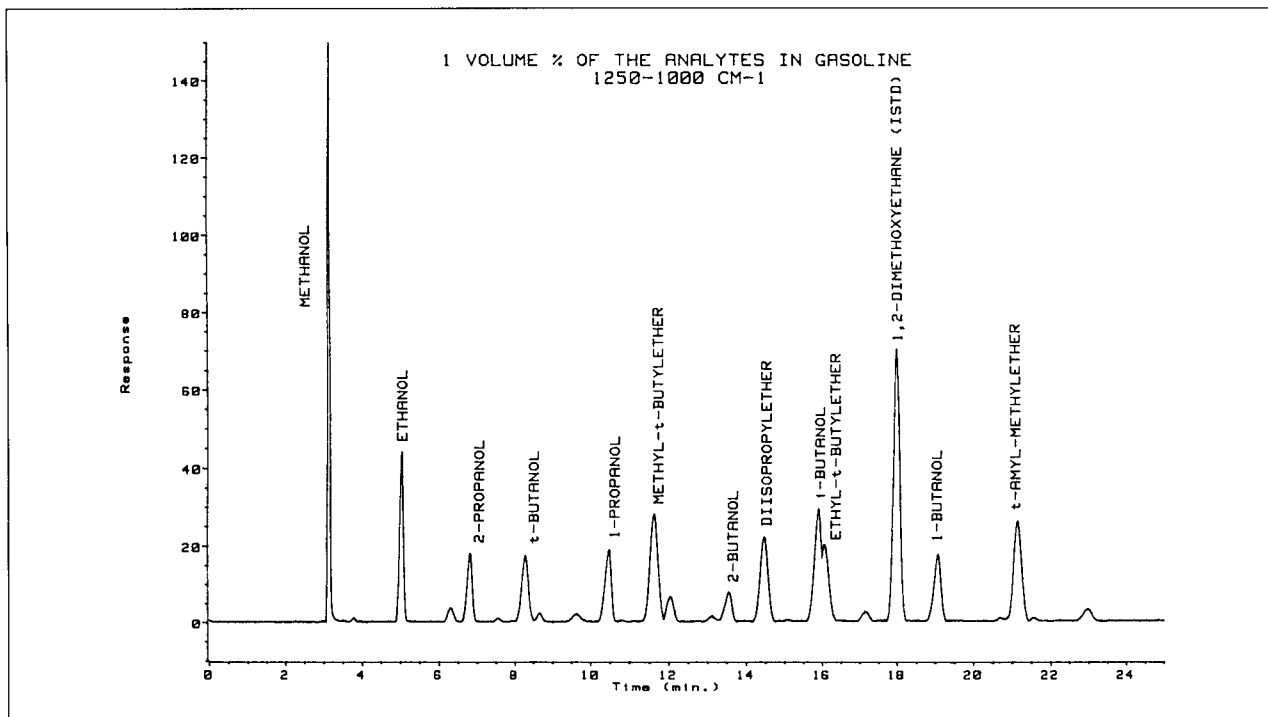


Figure 1. Oxygenate analytes and internal standard in gasoline at 1% by volume

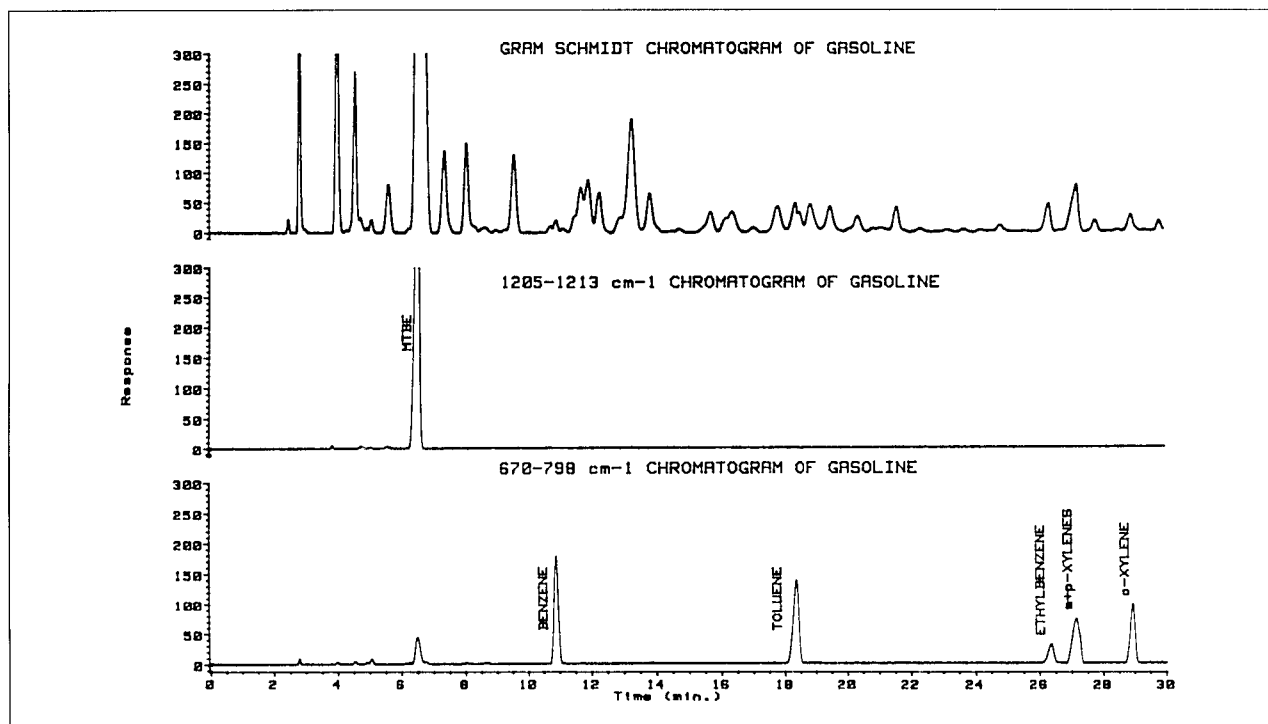


Figure 2. Gram Schmidt chromatogram for reformulated gasoline and selected wavelength chromatograms for MTBE and aromatics

quantitation is achieved using the internal standard calibration method. All calibration curves were linear with correlation coefficients  $\geq 0.999$ . The method had an average percentage accuracy of 1.0% and an average RSD of 0.5%. Precision and accuracy data are presented in Table 2.

The HP 5965B IRD is about 1/3 the size of an HP 5890GC. Figure 3 shows an IRD with the left side cover removed and the major parts of the system highlighted. Referral to this figure will aid in understanding the various experiments described below.

The first test performed was to determine if the FTIR could be moved from one location to another without affecting the calibrations. Calibration tests were made and the system was disassembled, the moisture sensitive interferometer and flow cell sealed in a mylar bag, and all the parts transported approximately 500 miles. The system was then reassembled and accuracy tests performed. These results are in Table 3. No significant change was observed in the percentage accuracy.

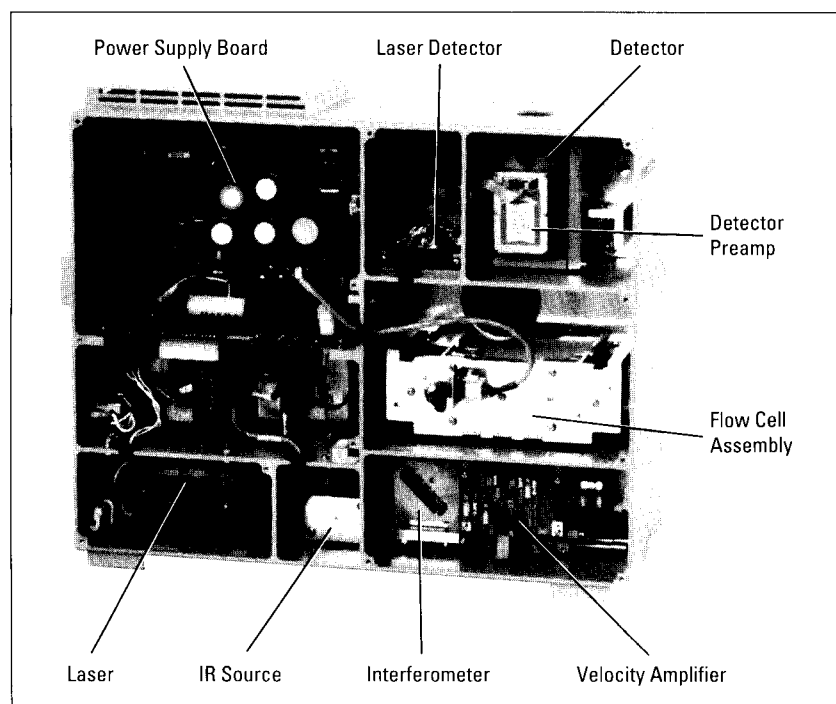
To determine which parts of the IRD would have an effect on the stability, all of the parts that could fail in the field (source, laser, MCT-detector, interferometer, and flow cell) were replaced one at a time with calibration

**Table 2. Precision and accuracy data**

Compound	Actual	Mean	RSD (n <sup>-1</sup> )	% Accuracy
MEOH	7.850	8.016	0.1	2.1
ETOH	7.800	7.865	0.1	0.8
2-PrOH	7.697	7.866	0.3	2.2
t-BuOH	7.581	7.538	0.2	0.6
1-PrOH	7.862	7.860	0.3	0.0
MTBE	7.316	7.315	0.1	0.0
2-BuOH	7.838	7.929	0.5	1.2
DIPE	7.138	7.222	0.1	1.2
i-BuOH	7.833	7.832	0.2	0.0
ETBE	7.364	7.399	0.1	0.5
1-BuOH	7.961	7.932	0.5	0.4
benzene	0.866	0.867	0.7	0.1
TAME	7.661	7.629	0.3	0.4
toluene	11.156	11.232	0.2	0.7
e-benzene	4.285	4.286	1.3	0.0
m-xylene	4.279	4.294	0.4	0.3
p-xylene	4.248	4.263	0.3	0.4
o-xylene	4.325	4.349	0.3	0.5

Average RSD = 0.3  
Average % accuracy = 0.6

n = 10  
Results are in grams/100 ml.



**Figure 3. Left side view of IRD**

---

## Conclusion

The HP GC/IRD was found to be very rugged and stable. Over a 10-month period in which approximately 1000 gasoline samples were injected at an oil company research laboratory, the IRD experienced 100% uptime. The interferometer and flow cell can be calibrated as a matched pair, moved to another system, and quickly set up for reformulated gasoline analyses. It has the potential to provide a significant savings in time and greatly improve the precision and accuracy of the data from different laboratories.

The authors would like to thank Al Gudat, Dominic DiUbaldo, and Ms. Lucinda Stude of the Hewlett-Packard Co.

## References

1. Diehl, J. W.; Finkbeiner, J. W.; and DiSanzo, F. P.; *Analytical Chemistry* 1992, 64, 3202-3205.

**Hewlett-Packard shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance or use of this material.**

**Information, descriptions and specifications in this publication are subject to change without notice.**

(23) 5091-6358E

Printed in the U.S.A. (1/93)