
The Use of GC/IR/MS for Determination of Oxygenated Compounds in Gasoline

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IRD Application Brief

HP 5965A Infrared Detector

IRD89-2

IRD Productivity Profile

Industry
Petroleum

Chemicals
Alcohol and ethers

Sample matrix
Automotive gasoline

Analysis
Qualitative and quantitative
determination of octane

The removal of lead antiknock compounds from gasoline in many countries around the world has resulted in the inclusion of oxygenated compounds such as low molecular weight ethers and alcohols as octane enhancers. For economic and environmental reasons, limits are often placed on the quantities of oxygenates allowed in unleaded gasoline. For example, the European Economic Community restricts the volume percentage of methanol (3%), ethanol (5%), i-propanol (5%), t-butanol (7%), and some ethers like t-butyl methyl ether (MTBE, 10%). These legal limits necessitate a reliable analytical method for the unambiguous identification and quantitation of the oxygenates in complex mixtures like gasoline. In this work, the HP 5965A Infrared Detector (IRD) is combined with the HP 5970B Mass Selective Detector (MSD) to conveniently characterize and quantify oxygenates in gasoline.

A gasoline sample was spiked with relevant alcohols and ethers in the mentioned concentration range. From a single injection, a total response chromatogram (TRC) from the IRD and a total ion chromatogram (TIC) from the MSD are shown in Figure 1. As can be seen in these chromatograms, the detectors differ in response for the various compound classes. The IRD response to aromatic compounds eluting in the latter part of the chromatogram is low compared to the MSD response due to relative weakness of aromatic infrared absorption bands.

On the other hand, the aliphatic compounds in the early part of the chromatogram are strong infrared absorbers and show intensities more comparable to the MSD. As a general rule, the MSD operating in the scanning mode detects 0.5 to 5 ng/compound while the IRD requires about 5 ng of a strong absorber

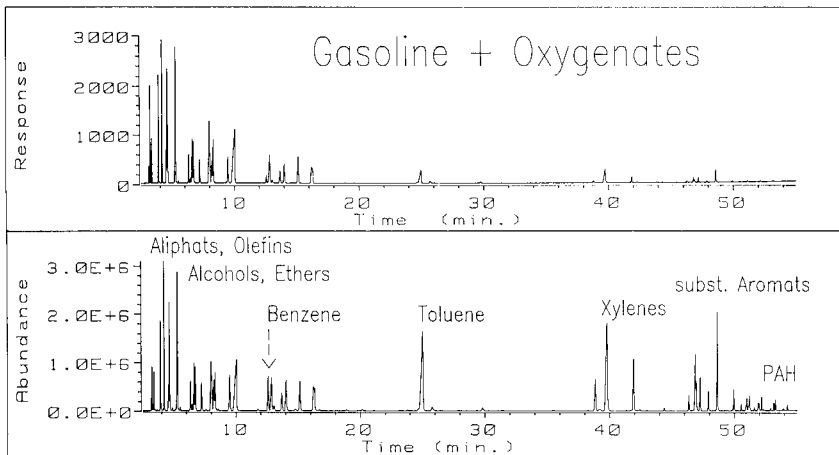


Figure 1. Gasoline sample. Top: IRD TRC; Bottom: MSD TIC

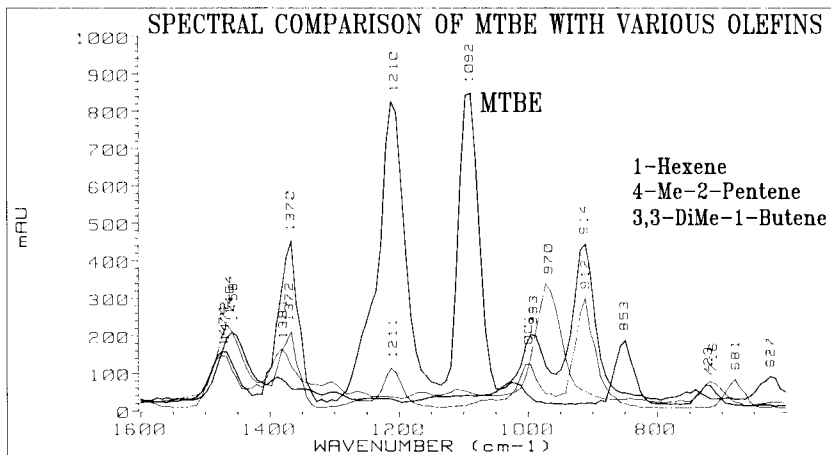


Figure 2. Spectral comparison of MTBE with olefins showing unique band at 1092 cm⁻¹

and 20 to 50 ng of a weak absorber to provide a chromatographic peak with a 5:1 signal-to-noise ratio. The ultimate sensitivity also depends to some extent on the chromatographic conditions and the sample matrix. For this work, the IRD and MSD were connected in series which means the MSD peaks lagged about 5 seconds behind the corresponding IRD peaks. A portion of the flow through the IRD is vented prior to the MSD resulting in a split ratio of approximately 5:1.

One of the complicating factors in a complex matrix like gasoline is the difficulty of separating chromatographically all the components in a reasonable amount of time. An advantage of this system is that complete separation is not always necessary to obtain valid results. In the case of MTBE, for example, there is often coelution with olefinic hydrocarbons in the gasoline. Figure 2 provides a spectral comparison of MTBE with several representative olefinic compounds. The MTBE is shown here to have a unique carbon-oxygen stretching band at 1092 cm⁻¹ which can be used to monitor this compound even when it coelutes with hydrocarbons.

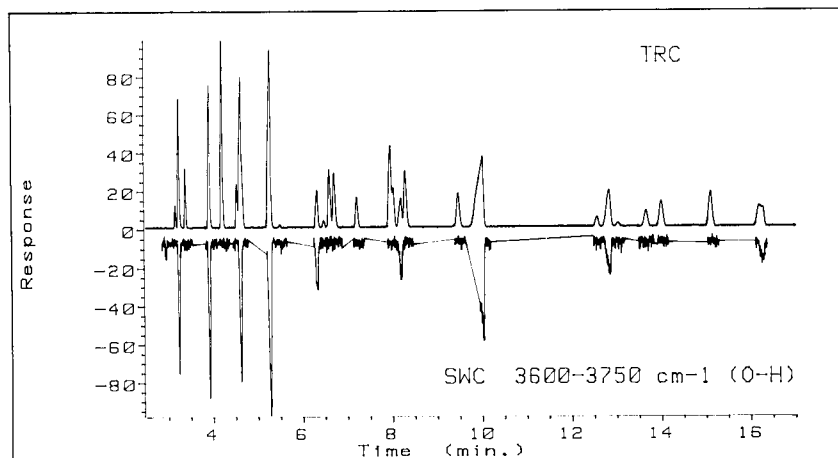


Figure 3. TRC and SWC for gasoline showing which peaks are alcohols

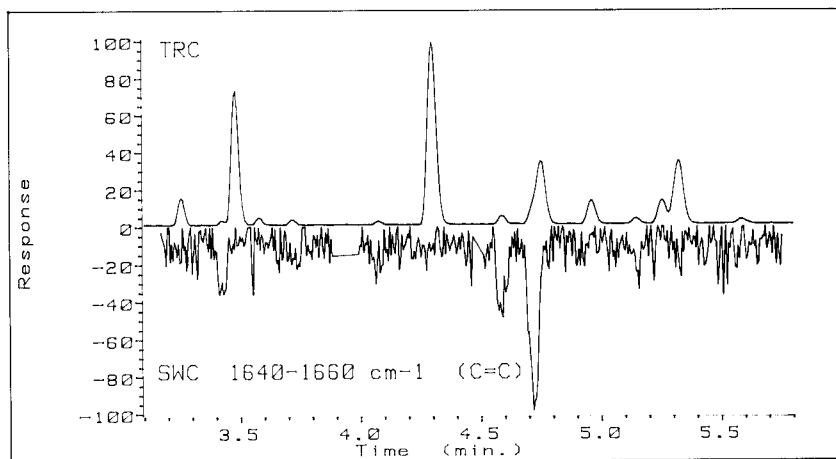


Figure 4. TRC and SWC for gasoline sample in which an olefin is coeluting with another compound at 4.75 minutes

This is easily accomplished by the IRD with a selected wavelength chromatogram (SWC) which is a standard software feature of the system. This is exemplified in Figure 3 showing the TRC for gasoline and the corresponding SWC in the O-H stretching region ($3600\text{--}3750\text{ cm}^{-1}$) indicating which of the peaks are alcohols.

The MSD nicely complements the IRD in helping to confirm the identity of unknowns, especially in the case of coelution. For example, in one of the gasoline samples an alkane coeluted with an olefin. This became apparent in the SWC shown in Figure 4 which reveals a compound containing a carbon-carbon double bond on the leading edge of the peak at 4.75 minutes. Obtaining spectra on each side of this peak and subjecting them to library searches on both the IRD and MSD confirmed the identities of the coeluting compounds as methylbutene and pentane as shown in Figure 5.

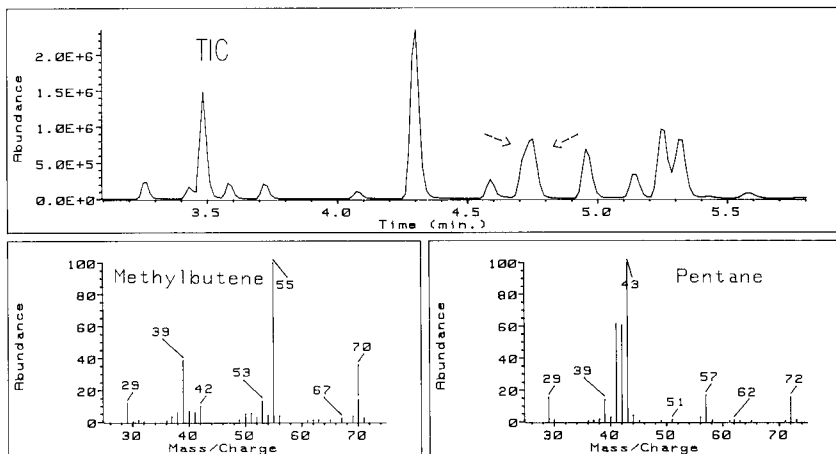


Figure 5. TIC and mass spectra for coeluting compounds at 4.75 minutes

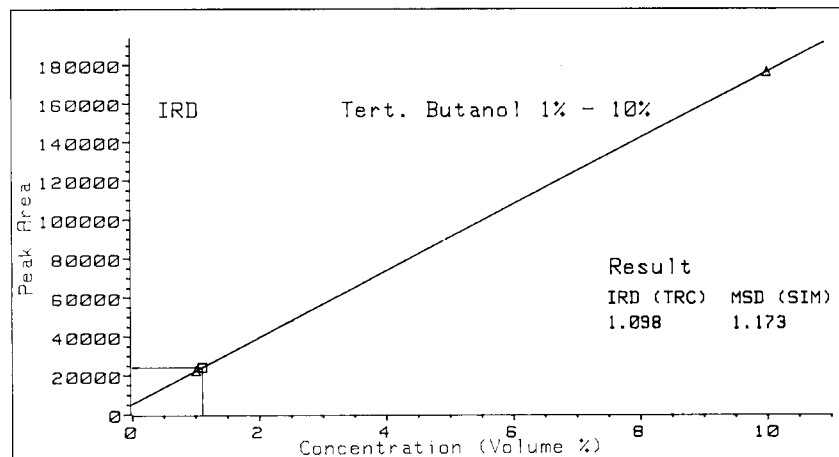


Figure 6. Calibration curve for IRD quantitation of t-butanol

Both the IRD and MSD provide integration and quantitation capability. To test and compare these capabilities of the combined system, t-butanol and benzene were identified and quantitated using the TRC from the IRD and the selected ion chromatogram from the MSD. The two completely independent quantitative results were shown to agree very well.

The calibration curve and result for t-butanol are shown in Figure 6 for the IRD/TRC method. The peak area response for t-butanol was 22336 giving a volume percent of 1.098. The MSD/SIM and IRD/TRC methods agreed within 0.2% for benzene and 6% for t-butanol. It should be pointed out that the SWC chromatograms can also be integrated allowing quantitation of oxygenates even in those instances when they are coeluting with hydrocarbon components.

Conclusion

The combined GC/IRD/MSD analytical system provides three dimensions of complementary data from a single injection of sample. Using the SWC, the IRD can conveniently screen for different compound classes. Previously identified compounds are reliably quantitated with the MSD SIM mode even in the low picogram range.

Conditions

Column

50 m HP 5 (5% phenyl methyl silicone), 0.32 mm id, 1 μ m film

Carrier Gas

He at 13 psi

Injection

1 μ l split 50:1, port temperature 250°C

Oven

35°C [1 min] to 45°C at 1°C/min to 70°C at 3°C/min to 250°C at 12°C/min

Light Pipe

250°C

IRD Transfer Lines

250°C

MS Transfer Line

250°C

IRD Resolution

8 cm^{-1}