

Accurate Analysis of Fuel Ethers and Oxygenates in a Single Injection without Calibration Standards using GC-Polyarc/FID

Application Note

Volatile Organic Compounds (VOCs)

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Abstract

The concentrations of oxygenates commonly used as fuel additives were determined with an average error of 1.7%, and within gravimetric uncertainties, using an ARC Polyarc[®] reactor in series with a flame ionization detector (FID) on a gas chromatograph (GC). The analysis demonstrates a greater than 5-fold speed-up of analysis with less cost and less introduction of human error. This method is applicable to a wider range of volatile organic compounds (VOCs) that have importance in environmental and industrial testing.

Introduction

Oxygenated compounds are added to fuels to increase octane number and allow for more complete combustion and less pollution. These have included C1-C4 alcohols (e.g., methanol and *tert*-butanol) and C5-C7 ethers (e.g., diisopropyl ether). The water solubility of these compounds has led to their presence in groundwater and soils around the world in areas where fuel leaks have occurred. Concerns about the presence of these compounds in aquifers and drinking water has led to the need for accurate testing and monitoring of their levels.

The analysis of oxygenates presents a unique challenge to the analytical chemist because of their varied response in GC detectors and the difficulty in preparing and handling volatile standards. Compounds are typically identified and quantified

using GC with mass spectrometry and 5-point calibration curves, such as those specified in EPA method 8260B for volatile organic compounds (VOCs), defined as those compounds with boiling points less than 200 °C. Accurate analysis requires expensive instruments and pumps, time-consuming 5-point calibrations, regular (sometimes weekly) purchases of standards, and the careful preparation, handling and storage of those standards. These requirements limit the feasibility and sometimes the accuracy of oxygenate analysis.

Here, we show that the accurate analysis of oxygenates and VOCs is possible without standards, using inexpensive GC/FID equipment and the Polyarc[®] reactor from Activated Research Company (ARC). The concentrations of six volatile ethers and alcohols are determined with an average error of 1.7% from a single injection and an arbitrary internal standard. These results provide a new avenue for environmental sampling that is quick and inexpensive while providing high accuracy.

Experimental

An Agilent 7890A GC equipped with a capillary-optimized FID and an ARC Polyarc reactor (PA-RRC-A02) were used for the analysis. Helium (99.999%, Praxair) was used for carrier and FID makeup. Air (zero grade, Praxair) and H₂ (99.999%, Praxair) were supplied to the ARC electronic flow control module (PA-MFC-A09) and to the FID. The effluent of the GC column was sent directly to the inlet of the Polyarc reactor via a zero-dead volume union (PA-CPM-R46). The reactor effluent was connected directly to the FID. Figure 1 illustrates the configuration.

A mixture of oxygenates (Restek, 30626, Lot A0115237) was transferred to a chilled (0 °C) sample vial for analysis. The sample was injected using an automated sample handler and a 10 µL syringe.



The sample was also analyzed without a Polyarc reactor on an identical setup, but with the FID H₂ flow rate at 35 sccm. In addition, the sample was analyzed using an Agilent 5973 mass spectrometer connected to the column effluent. Here, the end of the capillary

column was connected to a tee (Agilent, G3184-60065), which was connected to the inlet of the Polyarc/FID and the mass spectrometer via a retention gap column (Agilent, 160-2635-5, 2 ft., 0.1 mm ID).

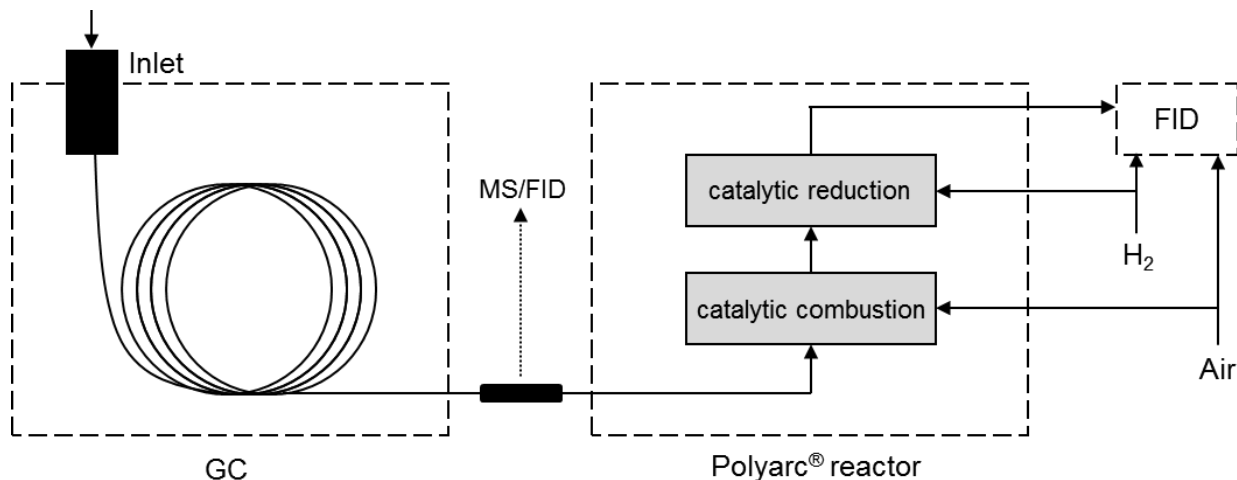


Figure 1. Diagram of GC setup with Polyarc/FID, FID and MS options.

GC conditions

Front inlet Split/splitless
 Inlet liner Agilent P/N 5190-2295
 Inlet Temperature 250 °C
 Inlet Mode 5:1 Split
 Inlet Pressure 11.27 psi
 Septum purge flow 3 sccm
 Oven 40 °C (2 min), 10 °C/min to 80 °C
 Column HP-5 (30 m × 0.32 mm × 0.25 μm)
 Syringe 10 μL
 Injection 0.2 μL

FID conditions

Temperature 315 °C
 H₂ 1.5 sccm
 Air 350 sccm
 Makeup 20 sccm (He)
 Sampling 100 Hz

Polyarc reactor conditions

Setpoint 293 °C
 H₂ 35 sccm
 Air 2.5 sccm

Results and Discussion

Table 1 describes the concentrations and elution order of alcohols and ethers in the mixture studied. The concentrations are reported as determined gravimetrically from the supplier. The unstressed (vial maintained at moderate temperatures) concentration uncertainties were 2.1 % for each component. The elution order was determined from the literature and confirmed with GC/MS. No other major components were observed. The concentration of methanol solvent was estimated from its density and the ideal volume of other species.

Table 1. Oxygenate sample information including elution order and concentration.

Elution	Short Name	Name	Concentration (μg/mL)
1	MeOH	Methanol	764225
2	TBA	Tert-butanol	9912
3	MTBE	methyl-tert-butyl ether	1986
4	DIPE	diisopropyl ether	1990
5	ETBE	ethyl-tert-butyl ether	1988
6	TAME	tert-amyl methyl ether	1988
7	TAEE	tert-amyl ethyl ether	1992

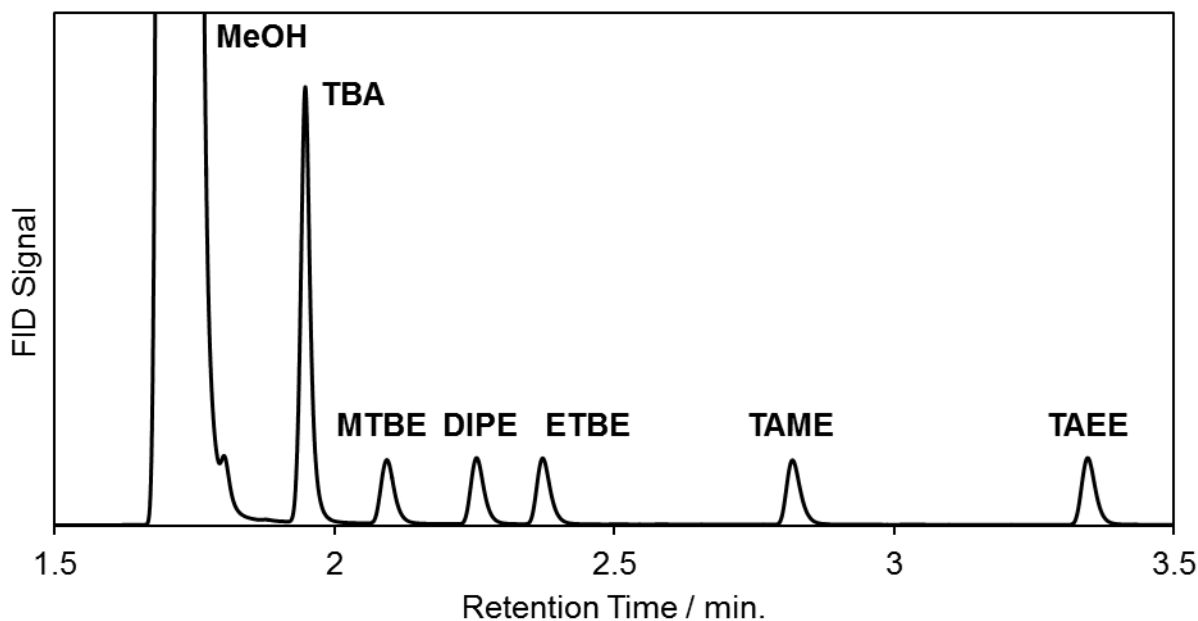


Figure 2. GC-Polyarc/FID chromatogram of oxygenates mixture.

Figure 2 shows the FID signal after Polyarc reactor conversion to methane of MeOH, TBA, MTBE, DIPE, ETBE, TAME, and TAAE. Baseline separation was obtained for all species. A small peak on the MeOH peak tail is most likely due to dimethyl ether formed from the reaction of MeOH on acid sites before chromatographic separation.

The Polyarc reactor converts compounds to methane in a two-step reaction scheme (Figure 1). First, compounds are oxidized until each carbon atom is converted to CO₂. Second, the resulting CO₂ is reduced to CH₄ in the presence of H₂. The resulting CH₄ is measured by the FID, and because non-carbon species are invisible to the FID, the resulting detector response and sensitivity is equivalent on a per carbon basis regardless of the original compound composition and type. The universal and uniform carbon response has been demonstrated on a variety of different molecules. The complete conversion of carbon to methane is the result of the special catalyst blend, reactor flow-path design, and the temperatures and conditions of the Polyarc reactor, and has been verified by mass spectrometry for a number of molecules and concentrations. Thermodynamic calculations ensure that >99.9% of carbon will become methane at equilibrium under the conditions of Polyarc operation [1].

The uniform response of the Polyarc/FID detector to carbon, allows for the quantification of species using,

$$RF = 1 = \frac{\text{area}/\text{concentration}}{\text{area}_{\text{standard}}/\text{concentration}_{\text{standard}}}, \quad (1)$$

where RF is the relative response factor of the species to the internal standard (IS), area is the integrated detector response, and concentration is the molar carbon concentration in the mixture. The RF is unity for all organic molecules when the Polyarc reactor is used. ETBE is used as the IS for this study, however, any component could be used (or added to the mixture) because of the uniform response of the Polyarc/FID to carbon. The concentration of alcohols and ethers in the sample are thus calculated from the carbon concentration of the IS and the relative peak areas of the IS and the analyte,

$$\text{concentration} = \frac{\text{area}}{\text{area}_{\text{standard}}} \text{concentration}_{\text{standard}} \cdot (2)$$

Sample calculation

The carbon concentration of ETBE in the undiluted sample can be calculated from its gravimetric concentration, 1988 µg/mL, molecular weight, 102.18 g/mol, and number of carbons per molecule, 6,

$$\frac{1987.92 \cdot 10^{-6} \text{ g ETBE}}{1 \text{ mL sample}} \cdot \frac{1 \text{ mol ETBE}}{102.18 \text{ g}} \cdot \frac{6 \text{ mol C}}{1 \text{ mol ETBE}}$$

$$= 116.73 \cdot 10^{-6} \text{ mol C/mL}.$$

The concentration of any other species can now be calculated from its area ratio to ETBE. For example, the integrated detector response (i.e., area under the curve) of MTBE is 740.2, whereas the area of ETBE is 770.7. From Eq. (2), we find that the carbon concentration of MTBE is,

$$\frac{740.2 \text{ pA} \cdot \text{s}}{770.7 \text{ pA} \cdot \text{s}} \cdot 116.73 \cdot 10^{-6} \text{ mol C/mL} = 112.1 \cdot 10^{-6} \text{ mol C/mL}$$

This equates to a measured concentration of 1977 $\mu\text{g/mL}$. The gravimetric concentration was 1986 $\mu\text{g/mL}$, yielding a total measurement vs. gravimetric error of,

$$\%Error = \frac{|1977 - 1986|}{1986} \cdot 100 = 0.5\%$$

Figure 3 shows the quantification errors using the GC-Polyarc/FID setup with Eq. (2) for the determination of compound concentrations from their FID peak areas. Absolute errors range from 0.5% for MTBE to 3.4% for tert-butanol. Five out of the six components (internal standard is not included) have quantification errors below the gravimetric unstressed uncertainty of sample preparation (<2.1%) from the manufacturer. The choice of internal standard has a negligible influence on average error values indicating the choice of internal standard is arbitrary because all components are converted to methane before detection.

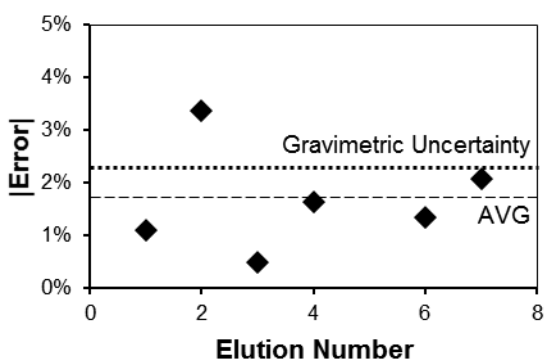


Figure 3. GC-Polyarc/FID quantification errors of compounds in Table 1. ETBE (elution number 5) is used as the internal standard. The dotted line represents the gravimetric unstressed uncertainty of the compounds and the dashed line represents the average of the measurement errors.

Figure 4 compares the actual and measured concentrations of all compounds. The concentrations span nearly three orders of magnitude from $\sim 10^3$ to $\sim 10^6$ $\mu\text{g/mL}$. This demonstrates the effective analysis range of the GC-Polyarc/FID from 1000 ppm to $\sim 100\%$ (pure solvent). Previous studies have shown detection sensitivity below 100 ppb with a similar setup indicating a linear dynamic range of about 7 orders of magnitude.

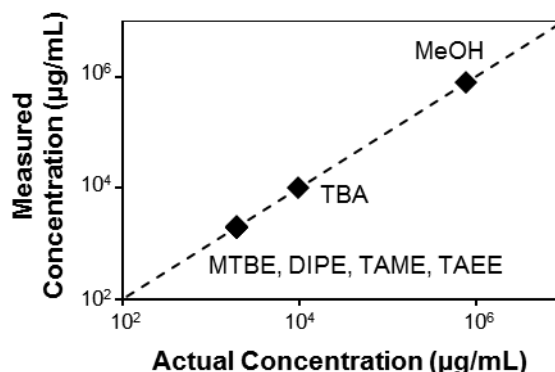


Figure 4. Parity plot of GC-Polyarc/FID measured and gravimetric (actual) concentrations of compounds in Table 1.

The concentrations of compounds in Table 1 could alternatively be determined with a similar accuracy using GC/FID or GC/MS (MeOH would saturate the MS) and five point calibration curves. The purchase and preparation of standards, and the subsequent calibrations, however, can represent a large investment in time and money. In this example a five point calibration curve for each of the 6 components relative to the internal standard would require 30 samples, or a 31-fold increase in the number of injections (97% reduction in samples with the Polyarc/FID). This could be reduced to 5 samples by using 7-component mixtures as standards, but the effort in producing these mixtures and the cost of the standards would be similar. In addition, there is a significant chance for the introduction of error during standard preparation and analysis. The use of GC-Polyarc/FID, even in tandem with GC/MS, represents a significant reduction in preparation and analysis cost and time.

The response factors of an FID have been tabulated for some compounds in the literature [2]. The accuracy of these relative response factors on various instruments with different operating conditions is unsubstantiated. The response factors of MeOH and TBA (other compounds are not available) have been reported as 0.23 and 0.74, respectively. Using these tabulated response factors with injections on the

GC/FID system leads to quantification errors of 28% for TBA.

The effective carbon number (ECN) concept was introduced to account for deviations in the response factors of the FID due to certain functional groups present in molecules. The ECN values published by Scanlon et al. [3] are commonly used to calculate relative response factors. Figure 5 shows the analysis error using the ECN method and FID peak areas from the injection of the mixture in Table 1 into a GC/FID (ETBE as the internal standard). Quantification errors range from 0.6% for MTBE to 44.2% for MeOH, with an average error of 10%. The ethers have an average analysis error of 1.6%, which is not surprising considering the similar relative responses of these species in the FID due to their similar ether functionality. TBA and MeOH have much higher errors of 9.5% and 44.2% suggesting the ECN model does not capture the different response of alcohols and ethers on this FID. These results strongly discourage the use of the ECN model when comparing alcohols and ethers.

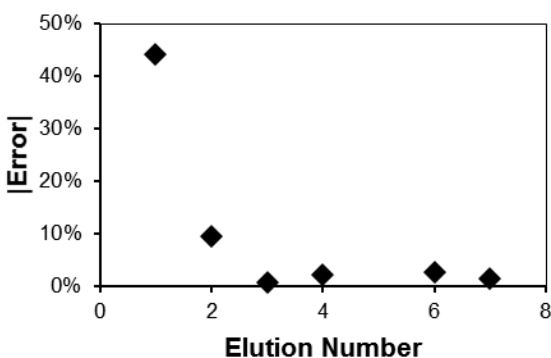


Figure 5. GC-FID quantification errors using the ECN model [3].

Conclusions

A 7 component mixture of oxygenates including ethers and alcohols commonly added to fuels was quantified using the GC-Polyarc/FID with an average error of 1.7% and concentrations that range over three orders of magnitude. This high accuracy is obtained without the use of calibrations, potentially reducing the analysts workload by more than 31-fold while maintaining exceptional accuracy. It is found that literature tabulated response factors and effective carbon numbers do not accurately reflect the different sensitivity of alcohols and ethers in the FID and should be avoided.

References

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2. Dietz, W. A., *J. Gas Chrom.*, 5 (1962) 68-71.
3. Scanlon, J. T., and Willis, D. E., *J. Chrom. Sci.*, 23 (1985) 333-340.

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For more information or to purchase a Polyarc[®] reactor, please contact us at 612-787-2721 or contact@activatedresearch.com.

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