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Nexis™ GC-2030 Gas Chromatograph

Application News

Analysis of Ethanol in E10 Gasoline Using Polyarc™ Microreactor for GC

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User Benefits

- Since the Polyarc microreactor converts all organic compounds to methane molecules, its detection sensitivity enables sensitive detection of the carbon concentration of samples.
- Polyarc reduces the work of preparing calibration curves for quantitative analysis of multiple compounds.
- Since Polyarc is a microreactor, sharp peaks can be obtained, and analysis of multiple compounds is also possible.

■ Introduction

The flame ionization detector (FID) can detect almost all organic compounds, and the sensitivity of the obtained chromatograms displays a correlation with concentration and number of carbon atoms in the compound. However, as a weakness of FID, its sensitivity decreases when an organic compound contains oxygen atoms, as in the case of alcohols.
The Polyarc microreactor improves sensitivity for alcohols and other compounds containing oxygen atoms (hereinafter, oxygenated compounds), allowing calibration using a single compound.
Research and use of biofuels has accelerated in recent years, and more sensitive quantitative analysis of oxygenated compounds in multiple compounds is now required.
This Application News introduces an example of an analysis of a sample simulating E10 gasoline, in which 10 % ethanol by volume concentration was added to gasoline, demonstrating that enhanced sensitivity for oxygenated compounds can be achieved by adding Polyarc to the instrument configuration. The accuracy of the quantitative analysis was also verified using a general standard sample (alkane).

■ E10 Gasoline

In recent years, E10 gasoline, which is produced by adding 10 v/v% ethanol to gasoline, has been considered an important sustainable biofuel from the viewpoints of reducing greenhouse gas emissions and improving energy efficiency.
Ethanol is an oxygenated compound that makes a negative contribution to FID sensitivity. Therefore, if ethanol is analyzed by the only conventional FID method, sensitivity will be lower than in analyses of compounds consisting of only ordinary hydrocarbons. This is based on the principle of the effective carbon number, as described later. In particular, it is difficult to analyze ethanol in samples such as gasoline, which contain many compounds, due to the effect of ethanol on analysis sensitivity. To avoid this problem, sensitivity responding to the carbon number can be obtained for all organic compounds by adding Polyarc, which converts all organic compounds to methane, thereby this enables higher sensitivity for compounds such as ethanol compared to using FID alone.
The technique described in this Application News is also applicable to E15 and E20 gasoline (containing 15 v/v% and 20 v/v% ethanol, respectively), which have been widely adopted in the United States and Brazil.

■ Polyarc Microreactor

Polyarc is a post-column type microreactor that is introduced between the column and the detector (FID). The organic compounds separated and eluted by the column are decomposed to methane by the Polyarc reactor in a two-stage oxidation-reduction reaction (Fig. 1). Since the decomposed methane is detected by the FID, the uniform sensitivity for the carbon number can be obtained, regardless of the type of functional groups in a sample.

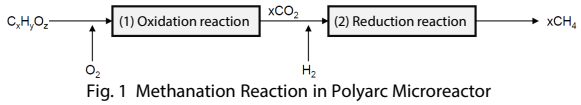

Fig. 1 Methanation Reaction in Polyarc Microreactor

Fig. 2 shows a schematic diagram of the instrument configuration and the appearance when Polyarc is installed. The reactor is arranged in the stage after the column but before the detector (FID), and is mounted on the top plate of the GC.

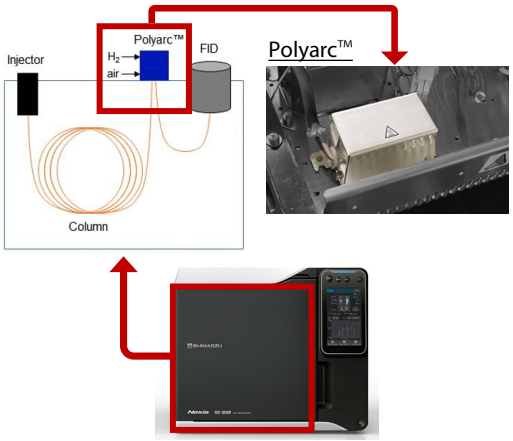

Fig. 2 Schematic Diagram and Appearance of Instrument Configuration Including Polyarc™

■ Effective Carbon Number

As mentioned above, the sensitivity of the FID detector varies depending on the types of functional groups in organic compounds. The detection sensitivity by the FID can be estimated based on the concept of the effective carbon number (ECN), which is an index showing how many carbon atoms in a compound function effectively. Depending on the type of functional groups contained in a compound, the carbon ratio in the molecule changes, and this causes changes in the sensitivity of the FID.
For example, both ethane (C_2H_6) and ethanol (C_2H_5OH) contain the same number of carbon atoms of 2, but the sensitivity of the FID for ethanol is only 75 % of its sensitivity for ethane because the primary hydroxyl group (-OH) behaves as -0.5 carbon atoms in terms of its contribution to the ECN. This means the ECN of ethanol is 1.5.
Table 1 shows several examples of other functional groups with ECNs lower than the number of carbon atoms.

Table 1 Examples of Functional Groups with ECNs Lower than Number of Carbon Atoms

Element	Orbital	Type of functional group	ECN contribution ratio
O	sp^3	Primary alcohol	-0.50
O	sp^3	Secondary alcohol	-0.75
O	sp^3	Tertiary alcohol	-0.25
O	sp^3	Ether	-1.00
N	sp^3	Primary amine	-0.60

On the other hand, since the Polyarc microreactor converts all the organic compounds to be detected to methane, variations in sensitivity due to differences in the functional groups can be eliminated. When analyzing oxygenated compounds such as alcohols, aldehydes, ketones, and carbonyls, the detection sensitivity of FID is generally a disadvantage in terms of the ECN. Therefore, enhanced detection sensitivity can be expected by adding the Polyarc reactor, particularly when analyzing oxygenated compounds.

■ Analysis Conditions

In this Application News, sensitivity for ethanol when the Polyarc was added and when using only the FID was compared using an E10 sample, in which 10 v/v% ethanol was added to gasoline, simulating a biofuel which has attracted attention in recent years, and quantitativity for ethanol was confirmed. In the quantitative analysis, it was also carried out by the external standard method using a hydrocarbon (dodecane; C12) with a concentration of 1 w/v% as a standard sample.

The analytical instrument was a GC-2030 (SPL/FID) model gas chromatograph with the Polyarc added (Fig. 2). Table 2 shows the analysis conditions.

Table 2 Analysis Conditions

Model	: GC-2030
Inj. Temp	: 250 ˚C
Inj. Mode	: Split 1:200
Carrier gas	: Helium
Column flow	: 1.0 mL/min
Column	: SH-I-5Sil MS (P/N 221-75954-30)
Column temp	: 35 ˚C (5 min) - 10 ˚C/min - 150 ˚C - 25 ˚C/min - 260 ˚C (15 min)
Detector	: FID
FID temp	: 320 ˚C
Makeup gas	: 24 mL/min
H_2 flow	: 1.5 mL/min
Air flow	: 200 mL/min
Polyarc temp	: 450 ˚C
Air Flow	: 2.5 mL/min
H_2 Flow	: 35 mL/min

■ Improvement of Sensitivity for Oxygenated Compound (Ethanol)

Fig. 3-1 shows a comparison of the chromatograms of an analysis of gasoline samples with and without addition of 10 v/v% ethanol. Fig. 3-2 shows the chromatograms with and without Polyarc, overlaying the respective analysis results. However, since the retention time is delayed by addition of the Polyarc, the time axis of the chromatogram obtained with the FID detector has been shifted 0.18 minutes (equivalent to 11.1 seconds) for this comparison.

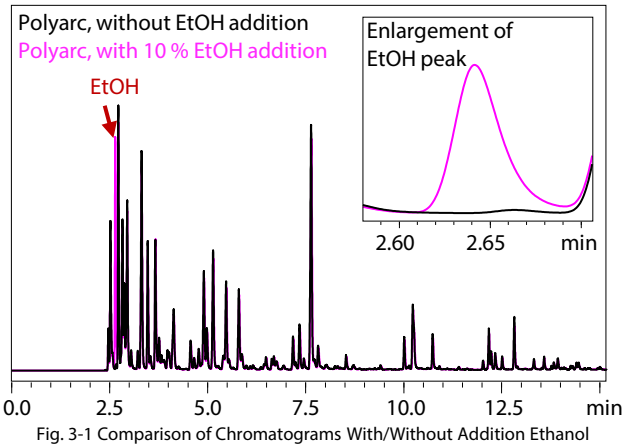

Fig. 3-1 Comparison of Chromatograms With/Without Addition Ethanol

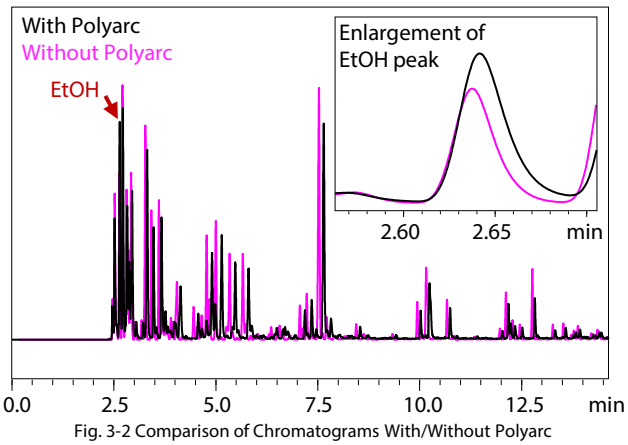

Fig. 3-2 Comparison of Chromatograms With/Without Polyarc

Table 3 Comparison of Peak Area Ratios of Ethanol/C12

	Area ratio (Ethanol/C12)	Sensitivity improvement of relative sensitivity for ethanol by using Polyarc
Polyarc	4.86	33 %
FID	3.66	-

In Fig. 3-1 and Fig. 3-2, the arrows indicate the peak of ethanol in the chromatograms, and enlarged chromatograms of the peaks of ethanol are shown in the inset at the right. From Fig. 3-2, it is clear that ethanol could be detected with higher sensitivity when Polyarc was added compared to when only FID was used. Table 3 shows a comparison of the ethanol peak area ratios (Ethanol/C12) obtained with Polyarc and FID, respectively, and summarizes the degree of sensitivity improvement of relative sensitivity by using the Polyarc.

According to Table 3, when Polyarc was added, the area ratio increased by 33 % compared to when only FID was used. This sensitivity improvement is based on the above-mentioned principle of the ECN. In terms of the ECN, compared to methane, which has an ECN of 1, ethanol was detected as equivalent to 1.5 molecules of methane (ECN of ethanol = 1.5) when only FID was used. However, when the Polyarc was added, ethanol was detected as equivalent to 2 molecules of methane (ECN = 2), which means the calculated sensitivity improvement by Polyarc is ideally 1.33 times that of FID. Thus, these results indicate that the actual values shown in Table 3 are in good agreement with the ideal value.

■ Quantitative Analysis Method Using Polyarc

As an example of a quantitative analysis of ethanol in E10 gasoline, this section introduces a quantitation method using the Polyarc reactor. The ethanol concentration of the samples used here is known. However, in order to verify quantitativity, on the assumption that this concentration is unknown, the ethanol concentration was calculated using C12 obtained with an external standard (E.S.) as the standard sample (the calculation was carried out by converting v/v% to w/v%, using the density information for ethanol). Table 4 shows the physical properties of the analytes and the area values obtained by the analysis.

Table 4 Comparison of Peak Area Ratios of Ethanol/C12

Compound	Molecular weight (g/mol)	Carbon number	Mass concentration (g/mL)	Area
Ethanol (target)	46.07	2	C_{EtOH}	2,178,535
C12 (E.S.)	170.33	12	0.01	447,604

When the Polyarc is added, sensitivity can be standardized in terms of the carbon concentration, and the mass concentration C_A of the sample to obtained can be calculated by Eq. (1):

$$C_A = C_S \times \frac{Area_A}{Area_S} \times \frac{\#C_S}{\#C_A} \times \frac{MW_A}{MW_S} \quad (1)$$

where:

C_A: Mass concentration of unknown sample,
C_S : Mass concentration of standard sample,
$Area_A$: Peak area of unknown sample,
$Area_S$: Peak area of standard sample,
$\#C_A$: Carbon number of unknown sample,
$\#C_S$: Carbon number of standard sample,
MW_A : Molecular weight of unknown sample,
MW_S : Molecular weight of standard sample.

If the numerical values in Table 4 are calculated by Eq. (1), C_{EtOH} = 0.0790 g/mL. Since the density of ethanol is 0.789 g/mL, it can be understood from the calculated value that the volume concentration of ethanol in the sample simulating E10 gasoline is 10 %. This means that quantitative calculation of samples with unknown concentrations is possible if at least one standard sample is available. This, in turn, means that quantitative analysis of multiple compounds can be achieved using a sample of one compounds, and quantitative analysis of compounds for which it is difficult to obtain a standard sample can also be achieved, regardless of the type of analysis sample.

■ Effect of the Polyarc Microreactor on Peak Width

As shown in the enlarged figure in Fig. 3-2, the peak width is broadened when Polyarc is added because the eluted compound passes through the reactor. However, any adverse effect on separation can be suppressed owing to the microstructural design of the Polyarc reactor.

Table 5 shows the results of a comparison of the peaks widths of ethanol and C12 when the Polyarc is added and with only FID. In the analysis of ethanol, the peak width increase due to addition of Polyarc was approximately 8 % as the halfwidth value, and when compared for the skirt part of the peak, the increase was approximately 10 % to 13 % (Table 5-1). For C12, the halfwidth increase was around 4 %, and the increase in the skirt part was about 2 % to 4 % (Fig. 5-2). Thus, satisfactory separation, similar to that without the Polyarc reactor, was obtained.

Based on these results, peak broadening due to the catalytic reaction in the microreactor was sufficiently suppressed and a sharp peak was obtained, indicating that separation of multiple compounds is also possible.

■ Conclusion

E10 gasoline was analyzed using an FID detector and an added Polyarc microreactor, confirming that oxygenated compounds can be analyzed with high sensitivity. This study also confirmed that a uniform reaction of organic compounds can be obtained in the FID, and peak broadening can be suppressed by standardizing the response of sensitivity.

Table 6 introduces several of the advantages that are possible by adding the Polyarc microreactor.

The Polyarc converts all organic compounds to methane having the same number of carbon atoms (mol), enabling high-sensitivity detection for compounds with low detection sensitivity by FID alone. In addition, since sensitivity is standardized, quantitation is possible using only one arbitrary calibration curve, regardless of the type of analysis compound. As a result, it is now possible to analyze compounds that were difficult to analyze by FID until now.

Table 5-1 Comparison of Peak Width of Ethanol

	Polyarc	FID	Difference of peak width (%)
Half-width (50 %)	0.027	0.025	8.0
Half-width (10 %)	0.053	0.048	10.4
Half-width (5 %)	0.062	0.055	12.7

Table 5-2 Comparison of Peak Width of C12

	Polyarc	FID	Difference of peak width (%)
Half-width (50 %)	0.028	0.027	3.7
Half-width (10 %)	0.054	0.052	3.9
Half-width (5 %)	0.063	0.062	1.6

Table 6 Advantages by Addition of Polyarc

Case	Effects of Polyarc
In multiple compounds analysis, it is necessary to prepare multiple calibration curves, which is tedious, time-consuming work.	Quantitative analysis is possible with a single calibration curve (or the number of calibration curves can be reduced).
Want to analyze multiple compounds samples.	Separation is satisfactory for obtaining sharp peaks.
Already conduct quantitative analysis by ○○ conversion, and have reduced the number of calibration curves.	Polyarc can also improve sensitivity.
Qualitative/quantitative analysis of oxygenated compounds and heteroatom compounds is not going well.	Polyarc eliminates differences due to functional groups, improving sensitivity.
Want to analyze formic acid, formaldehyde, CO, and CO_2 by GC-FID.	All organic compounds are converted to methane, and therefore can be detected by FID.
Cannot obtain standard substances for calibration curves of target compounds for quantitative analysis.	Arbitrary inexpensive standard substances can be substituted for hard-to-obtain standard substances.

01-01033-EN First Edition: Oct. 2025

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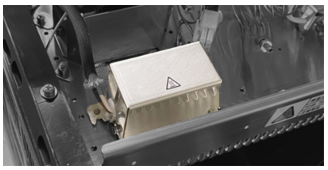

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