Accurate and Repeatable CO_2 Analysis Using a Jetanizer on a Shimadzu 2030 GC

Application Note

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Gas Analysis

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Abstract

The flame ionization detector (FID) has no response to carbon dioxide (CO_2) under normal conditions without conversion to a more suitable compound for detection, such as methane. In this application note, we show accurate analysis of CO_2 using an FID configured with a Jetanizer™, a catalytic reactor contained fully in the FID jet, relative to a known concentration of pentane.

Introduction

The FID detects CHO^+ ions formed during combustion of organic molecules in a hydrogen/air flame. Detection requires the molecule to contain carbon – hydrogen bonds, so compounds including CO and CO_2 cannot be detected with the FID alone. The thermal conductivity detector (TCD) is often used for CO and CO_2 analysis, but low-level detection is limited to 10^{-9} g/s, which is orders of magnitude less sensitive than the FID, which can detect 10^{-12} g C/s. Because of this improved sensitivity there is great interest in using the FID for this analysis in markets including air monitoring, waste analysis, environmental analysis, reaction monitoring, and more. Methanizers have been used since 1965 to convert CO and CO_2 to methane using a nickel catalyst to allow for their detection in the FID. These methanizers are easily poisoned by small amounts of sulfur, and deactivation can occur with air and light compounds such as acetylene or ethylene. Methanizers are also difficult and time consuming to install, maintain, and operate. Installing a methanizer requires creating additional column connections to the reactor, supplying an additional hydrogen gas flow, and precisely controlling an additional, isothermal, high temperature zone. When the catalyst is deactivated, the methanizer assembly must be disassembled and the catalyst tube re-packed, which can be a tedious task. Since the methanizer is generally installed as an add-on feature, proper warm-up and conditioning parameters are not automated must be processed manually allowing for more opportunity for the catalyst to be deactivated or poisoned. Because of these difficulties, methanizer-FID configurations are often on dedicated instruments, and maintenance or installation can put instruments out of commission for an entire day or more.

In response to feedback from customers using methanizers, ARC developed the Jetanizer, which is an FID jet that performs in situ methanation (i.e., inside of the jet itself). The Jetanizer is 3D-printed with stainless steel to maximize the methanation reaction rate and to create geometries that minimize band broadening. A schematic of the Jetanizer and the reaction that it performs is shown in Figure 1. Hydrogen is supplied by the FID (similar to a normal FID jet), and this mixes with the analytes as they enter the Jetanizer. CO and CO_2 are subsequently converted to methane, which then passes directly to the FID where it is detected.

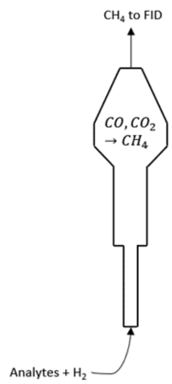

Figure 1. Schematic of the Jetanizer

Figure 2. Shimadzu 2030 GC

Experimental

A Shimadzu 2030 GC equipped with a split/splitless inlet, a VICI six port gas sampling loop with a 250 µL sample loop, a Jetanizer (ARC [JT-SHZ-CP2]), and a flame ionization detector was used for the analysis. Helium (99.999%, Praxair) was used for carrier and FID makeup. Air and H_2 supplied via a VICI DBS generator were supplied to the FID. The GC column was connected directly into the Jetanizer. A cylinder of 1.007 ± 0.02 mol% CO_2 and 0.1997 ± 0.004 mol% pentane in nitrogen (Airgas X03HE98C15A9996) was connected to a flow meter to control 2.5 sccm flowing through the sample loop.

GC conditions

Front inlet	Split/splitless
Inlet temperature	250 °C
Inlet liner	Shimadzu 227-35008-01
Carrier gas	He; 2.6 sccm constant flow
Septum purge flow	3 sccm
Oven	40 °C isothermal
Column	HP-5MS UI (30 m × 0.25 mm × 0.25 µm)
Sample loop volume	250 µL
Inlet Split Ratio	10:1

FID conditions

Temperature	400 °C
H_2	35 sccm
Air	350 sccm
Makeup	24 sccm (He)

Analysis Procedure

Carbon dioxide was quantified relative to pentane using the Jetanizer. The molar concentration was calculated using the following equation. Methane produced from reduction reaction in the Jetanizer was measured with the FID, resulting in an equimolar carbon response. The concentration can therefore be calculated using the ratio of the analyte to the internal standard using the following equation:

$$C_A = C_s \left(\frac{Area_A}{Area_S}\right)\left(\frac{\#C_S}{\#C_A}\right)$$

where:

C_A = Molar concentration of analyte
$Area_A$ = Integrated peak area of the analyte
$Area_S$ = Integrated peak area of the standard
$\#C_S$ = Number of carbon atoms for standard
$\#C_A$ = Number of carbon atoms for analyte

More Details can be found within the "Quantification with the Polyarc.pdf" on the web at https://www.activatedresearch.com/documents/

Results and Discussion

Ten replicate injections of the standard gas mixture were done over a 30-minute period. Carbon dioxide eluted first, followed by pentane. Table 1 shows relative standard deviations and average area counts for the two compounds over the ten runs. The molar concentrations are such that the areas should be nearly equal. Table two shows quantification results reflecting a less than 2% error when quantifying CO_2 with pentane as an internal standard.

Table 1. Relative Standard Deviations

Compound	Average Area (pA-s)	RSD
CO_2	1640170	0.13%
Pentane	1603699	0.14%

Table 2. Quantification Results

Compound	Gravimetric Concentration (mol%)	Measured Concentration (mol%)
CO_2	1.007 ± 0.02	1.021
Pentane	0.1997 ± 0.004	N/A (IS)

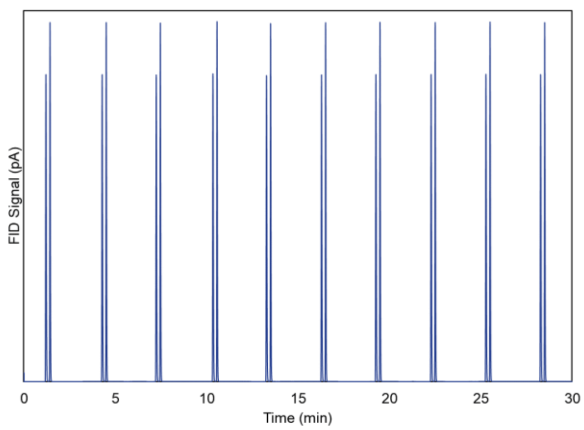

Figure 3. Chromatogram of 10 Injections

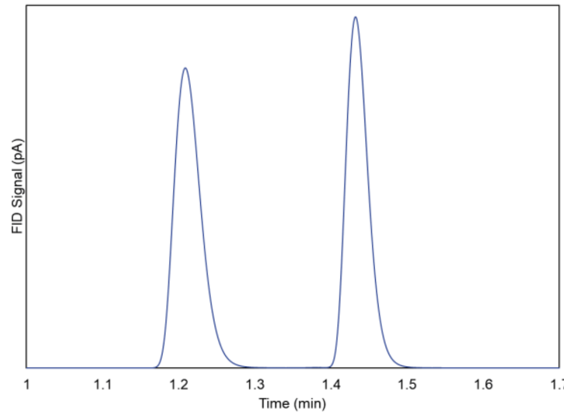

Figure 4. Single Injection Chromatogram

Figures 3 and 4 show the chromatograms of all ten injections and a single injection, respectively. The repeatability of the injections can be visualized here, and good peak shape is also shown.

Conclusions

The capability of the Shimadzu 2030 GC/FID system was expanded to accurately and reproducibility measure carbon dioxide at a concentration of 1 mol%. Relative standard deviations of CO_2 and pentane were well within typically accepted criteria, and the quantification error of 1.4% is within the reported error of 2% on the standard cylinder. With this technique, the Shimadzu 2030 GC can easily be configured to detect CO_2 accurately in industries such as air monitoring, drinking water, reaction monitoring, TOGA, and more.

Contact Us

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

Please visit our website for details and additional technical literature.

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