

Investigating $^{13}\text{C}/^{12}\text{C}$ Isotope Ratios of Methane-Pentane in Natural Gas by GC-IRMS

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Key Words

Compound Specific Isotope Analysis, Natural Gas, Methane, GC Combustion, Isotope Ratio MS

Introduction

Natural gas is produced by biodegradation and by thermal degradation of organic matter. The isotope ratios of compounds in natural gas can hold information about the substrate and the degradation processes. The $^{13}\text{C}/^{12}\text{C}$ isotope ratios of all components in natural gas, including methane, can be analyzed within the same GC-IRMS run. In GC-IRMS, all carbon-bearing compounds eluting from a GC are converted on-line into CO_2 in the combustion interface and are transferred on-line to the IRMS.

Methane (C_1), a trace gas in air but the dominant component in natural gas is difficult to combust.^{1,2} The high concentration of C_1 versus the low concentration of ethane to pentane ($\text{C}_2\text{-C}_5$) requires that the IRMS have a large dynamic range. This usually leads to two separate analyses of methane and of the minor components. The Thermo Scientific[™] combustion interfaces like the here used GC/CII interface followed by GC/CIII and GC Isolink in combination with Thermo Scientific IRMS allow analyses of $\text{C}_1\text{-C}_5$ within one run by combining highest sensitivity, linearity and stability with a wide dynamic range and chromatographic integrity.

Results

Methane requires higher combustion temperatures which usually result in a fast loss of oxygen from combustion reactors containing only CuO . This creates uncertainties for continuous methane analyses. A combination of nickel and copper oxides in a capillary design, however, allows higher temperatures without these negative effects. Above 940°C > 99.97% of the methane is combusted (Figure 1); beyond 960°C no significant change in the δ -value can be detected (Figure 2). The standard deviation within $960\text{-}1020^\circ\text{C}$ in this study is $\pm 0.026\%$. The combustion reactors in the GC/C II interface and its successors allow to use these operating conditions routinely.

Figure 3 shows a chromatogram for methane analysis in natural gas. The peak intensities ranged from 60 mV to 9700 mV representing a dynamic range of 1 to 150. The $\delta^{13}\text{C}$ value of methane, at 9700 mV, was $-49.050 \pm 0.036\%$ and the mean standard deviation of all the minor components was 0.223%. n-C5 and i-C5 were calculated with an optimized background algorithm to account for column bleed. These data clearly demonstrate the wide dynamic range, linearity and stability of both the Thermo Scientific IRMS and the combustion interfaces.

Similar results can be expected from a Thermo Scientific Delta V[™] IRMS or Thermo Scientific MAT 253[™] IRMS coupled with the Thermo Scientific GC Isolink[™] II via the Thermo Scientific ConFlo[™] IV universal interface.

Method

Injector	split/splitless (split 1:70)
Cap. column	Poraplot Q, 25 m, 0.32 mm i.d.
GC program	4 min at 26°C , $5^\circ\text{C}/\text{min}$ to 180°C , 5 min at 180°C
GC/C interface	Standard GC/C II interface oxidation reactor at 980°C , reduction reactor at 600°C

Table 1. GC-IRMS parameters.

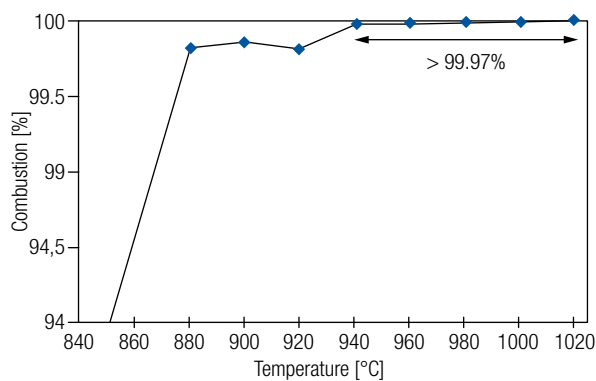


Figure 1. Methane, % combustion vs. T [°C].

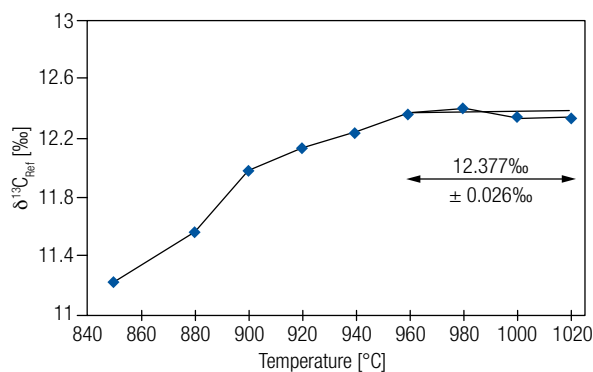


Figure 2. Methane, δ¹³C_ref [‰] vs. T [°C].

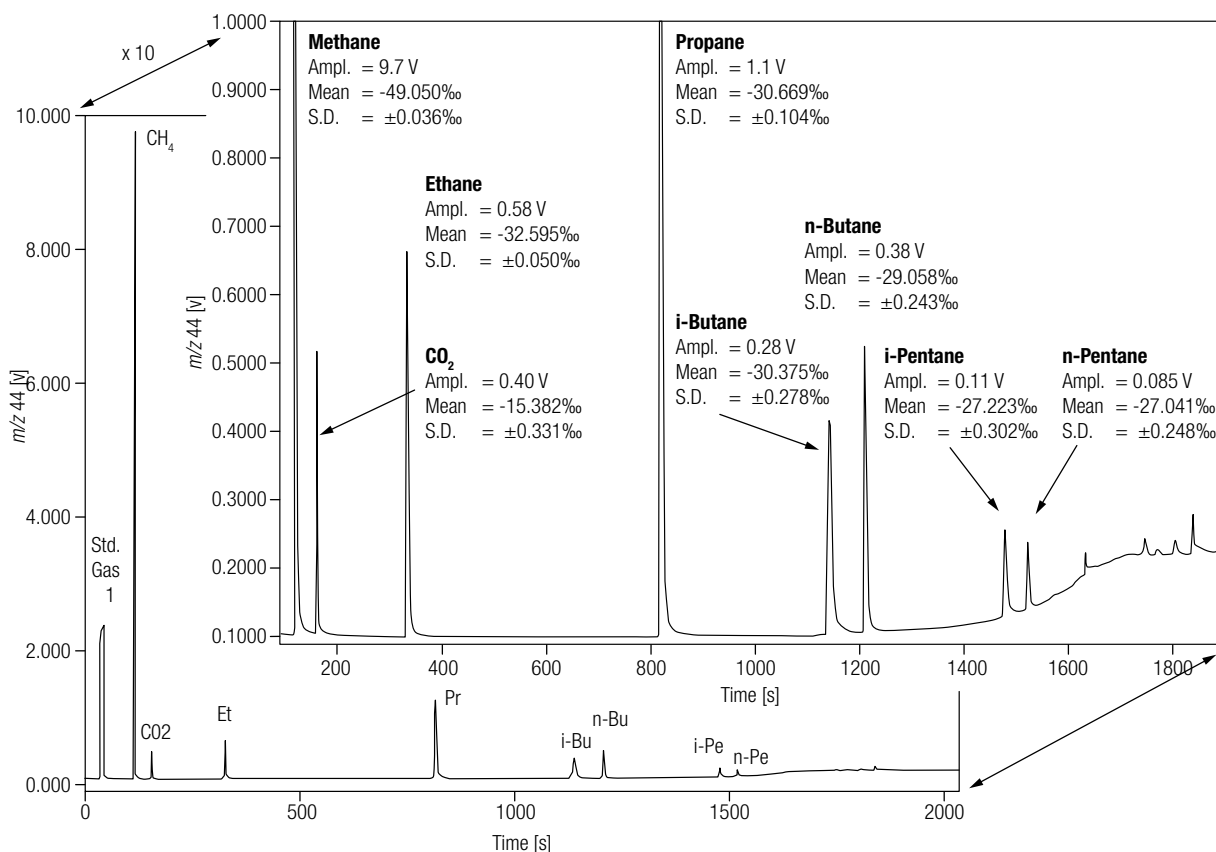


Figure 3. GC-IRMS analysis of natural gas.

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