

Original

# Development of a Precise Method for the Quantitative Analysis of Hydrocarbons Using Post–Column Reaction Capillary Gas Chromatography with Flame Ionization Detection

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## Abstract

In a gas chromatograph with a flame ionization detector (GC/FID) measurement, standard materials for each target compound are essential for quantitative analysis. In order to decrease the number of required calibration standards, a post–column reaction GC/FID system was developed. In this system, two micro–reactors were attached to a capillary GC/FID system in order to convert the target compounds into methane. High precision sample gas mixtures and solutions were prepared by gravimetric methods and used to perform accurate evaluations of the developed system. Because all target compounds were converted to methane, quantitative analysis of the samples on the developed system could be carried out by using any of the compounds as an internal standard. The results showed excellent agreement with the prepared concentrations and analytical values. These results indicated that this post–column reaction GC/FID system was a useful method for the precise quantitative analysis of carbon monoxide, carbon dioxide, and hydrocarbons.

*Keywords:* post–column reaction, micro–reactor, oxidation, reduction, hydrocarbon, quantitative analysis, GC/FID, standard material.

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## Introduction

Gas chromatographs equipped with flame ionization detectors (GC/FID) are widely used for the quantitative analysis of hydrocarbon compounds. For precise quantitative analysis, it is essential to calibrate the GC/FID system using calibration standards for each analyte. This is both inefficient and cost–prohibitive. The response factor method is also used for calibration of the GC/FID. The response factor is determined by the analysis of standard materials or other methods prior to measurement of the analytes. It is known

that the FID response for hydrocarbons is generally proportional to the carbon number of the analyte. When the large number of hydrocarbons needs to be analyzed, for example fuel or oil in petroleum field, the response factor is determined by using the carbon number, then used for calibration of the GC/FID.<sup>1–3</sup> Unfortunately, the response of the FID is not exactly proportional to the carbon number but is influenced by the functional groups of the analytes, the structure of the hydrocarbons, and the operating conditions of the FID.<sup>4–10</sup> For these reasons, if a complex mixture is calibrated by

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the response factor, the experimental result may vary greatly from the true value.

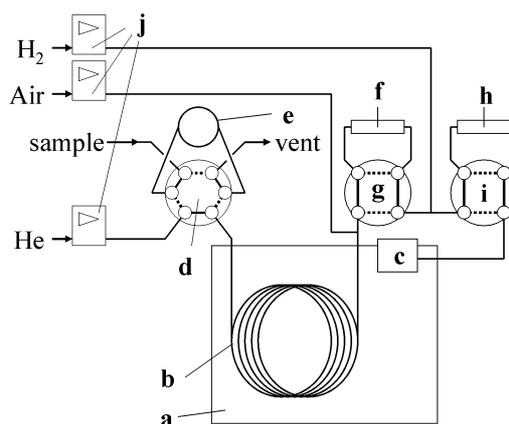
In order to decrease the number of required calibration standards and avoid the influence of the operating conditions of the FID, a post-column reaction GC/FID system was developed and evaluated. In this system, two micro-reactors are attached to a capillary GC/FID system. The first micro-reactor oxidizes the analytes in GC effluent to carbon dioxide. The second micro-reactor reduces carbon dioxide to methane. Thus, the target compounds in the sample are separated by GC and then detected as methane. This detection system is already used on the nonmethane organics (NMO) analyzer in EPA method 25, in which total nonmethane volatile organic compounds are quantified as methane.<sup>11</sup> However, the NMO analyzer is not capable of analyzing each organic compounds quantitatively. Our post-column reaction gas chromatograph system was designed in order to quantify organic compounds after GC separation. In our system, only one standard material, e.g., methane is sufficient for the calibration. Our system is also equipped with a simple validation mechanism to evaluate the efficiencies of the oxidation and reduction reactions. The reaction efficiency was determined by using primary standard materials that had been prepared precisely by gravimetric methods,<sup>12</sup> and values of the concentrations of these prepared samples were used as reference values. Quantitative analysis of test compounds was carried out with the new system using one of the compounds in the samples as an internal calibration standard, and the analytical results were compared with the reference values. Such calibration method is defined as primary ratio method.<sup>13</sup>

In this report, we demonstrate hydrocarbons as an example which shows proportional response to the carbon number by our system.

## Experimental

### Instruments

Measurements of gaseous samples were performed on an HP 5890 gas chromatograph (Agilent Technologies, Wilmington, DE, USA) equipped with a 6-port gas sampling valve and an FID, and measurements of liquid samples were performed on an Agilent 6890 gas chromatograph (Agilent Technologies) equipped with a cool on-column inlet, an Agilent 7683 B automatic liquid sampler, and an FID. A schematic diagram of the instrument for gaseous samples measurements was shown in Figure 1. An HP-PLOT Al<sub>2</sub>O<sub>3</sub> "M" capillary column (Agilent Technologies), a Carboxen-1006 PLOT capillary column (Sigma-Aldrich Co., St. Louis, MO, USA), and a SOLGEL-WAX capillary column (SGE International Pty. Ltd., Victoria, Australia) were used for the separation. To avoid uncertainties during the sample loading process, e.g., the possibility of partial separation on the injector and imperfect va-



**Figure 1.** Schematic diagram of the post-column reaction GC/FID for gaseous samples. **a:** gas chromatograph; **b:** capillary column; **c:** detector (FID); **d:** gas sampling valve (6-port valve); **e:** gas sampling loop; **f:** micro-reactor for oxidation; **g:** bypass valve (4-port valve) for the micro-reactor **f**; **h:** micro-reactor for reduction; **i:** bypass valve (4-port valve) for the micro-reactor **h**; **j:** thermal mass flow controllers.

porization of the sample, the gaseous sample was injected directly by a gas sampling valve and gas sampling loop, and an on-column injection method was used for liquid sample injection. These injection methods are very precise injection methods with low uncertainties in the injection reproducibility. The operating conditions of the GC/FID system are summarized in Tables 1 and 2. The micro-reactor consisted of a stainless tube with catalyst, a heater block, and a temperature controller. The oxidation catalyst, palladium-asbestos (Wako Pure Chemical Industries, Ltd., Osaka, Japan), was packed into the stainless steel tube (OD: 1.58 mm, ID: 0.75 mm) of the first micro-reactor **f**. The reduction catalyst, nickel catalyst for

**Table 1.** Operating conditions of GC/FID for gaseous samples

Gas chromatograph	HP 5890
Injection method	Direct injection using 6-port sampling valve
Sample volume	100 $\mu$ L
FID condition	
Fuel gas*	H <sub>2</sub> : 38 mL min <sup>-1</sup> Air: 400 mL min <sup>-1</sup>
Makeup gas	He: 25 mL min <sup>-1</sup>
FID temperature	250 °C
For separation of gas mixtures <b>1, 2, 3, and 4</b>	
Column	HP-PLOT Al <sub>2</sub> O <sub>3</sub> "M" (50 m $\times$ 0.32 mm i.d., 8 $\mu$ m thickness)
Column flow	He: 2.8 mL min <sup>-1</sup>
Oven temperature	80 °C
For separation of gas mixture <b>5</b>	
Column	Carboxen-1006 PLOT (30 m $\times$ 0.53 mm i.d.)
Column flow	He: 2.8 mL min <sup>-1</sup>
Oven temperature	50 °C

\* These values include the volume of added oxidizing/reducing reagent.

**Table 2.** Operating condition of GC/FID for liquid samples

Gas chromatograph	Agilent 6890
Injection method	On-column injection with automatic liquid sampler
Sample volume	0.1 $\mu\text{L}$
Column	SOLGEL-WAX (60 m $\times$ 0.25 mm i.d., 0.25 $\mu\text{m}$ thickness)
Column flow	He: 3.0 mL min <sup>-1</sup>
Oven temperature	An initial hold of 2 min at 35 $^{\circ}\text{C}$ , 5 $^{\circ}\text{C}/\text{min}$ until 165 $^{\circ}\text{C}$ , 15 $^{\circ}\text{C}/\text{min}$ until 225 $^{\circ}\text{C}$ , and then hold 4 min at 225 $^{\circ}\text{C}$ .
FID condition	
Fuel gas*	H <sub>2</sub> : 40 mL min <sup>-1</sup> Air: 450 mL min <sup>-1</sup>
Makeup gas	He: 40 mL min <sup>-1</sup>
FID temperature	250 $^{\circ}\text{C}$

\*These values include the volume of added oxidizing/reducing reagent.

methanizer (GL Sciences Inc., Tokyo, Japan), was packed into the stainless tube (OD: 3.17 mm, ID: 1.39 mm) of the second micro-reactor **h**. Both reaction tubes were plugged with quartz wool. Two 4-port valves were used to bypass the micro-reactors in order to check their performance. Carrier and reaction gases were controlled with thermal mass flow controllers (SEC-400MK3, HORIBA STEC Co., Ltd., Kyoto, Japan).

#### Chemicals

Methane was purchased from Tokyo Gas Chemical Co., Ltd. (Tokyo, Japan). Propane was purchased from Takachiho Chemical Industrial Co., Ltd. (Tokyo, Japan). Carbon monoxide was purchased from Taiyo Toyo Sanso Co., Ltd. (Tokyo, Japan). Nitrogen, helium, and carbon dioxide were purchased from Nippon Sanso Co., Ltd. (Tokyo, Japan). Ethylbenzene, *n*-dodecane, and acetone were purchased from Wako Pure Chemical Industries, Ltd. *n*-Hexadecane was purchased from Aldrich Chemical Company, Inc.

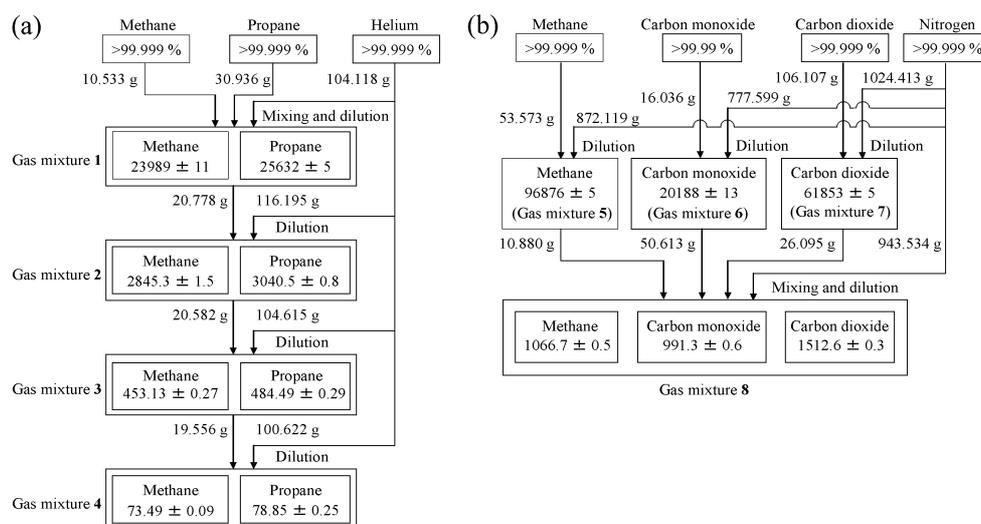
**Table 3.** Chemical purities

Compounds	Purities (%)
Methane	>99.999
Carbon monoxide	>99.99
Carbon dioxide	>99.999
Propane	>99.999
<i>n</i> -Dodecane	99.83
<i>n</i> -Hexadecane	99.08
<i>n</i> -Eicosane	99.75
Ethylbenzene	99.57
Nitrogen	>99.999
Helium	>99.999
Acetone	99.95

(Milwaukee, WI, USA). *n*-Eicosane was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Purities of all chemicals were analyzed and specified by ourselves, and summarized in Table 3.

#### Preparation of high precision gas mixtures using gravimetric method

High precision sample gas mixtures were prepared in 9.4 L aluminum alloy cylinders at the high accuracy gas preparation facility in our institute which was designed to prepare primary standard gases.<sup>14</sup> Before weighing the cylinder, cylinder temperature was stabilized for 2 hours in the balance room. Standard uncertainties<sup>15</sup> for the concentrations of the sample gas mixtures for this study were less than 0.4% and had enough precision to evaluate the reproducibility of GC/FID measurements. Schematic diagrams of the preparation procedure of the gas mixtures were shown in Figure 2. Gas mixtures **3**, **4**, **5**, **6**, and **7** were prepared similarly to gas mixture **2**.



**Figure 2.** Schematic diagrams of preparation of sample gas mixtures by gravimetric method. Units of the values (mean  $\pm$  standard uncertainty) of the concentrations were  $\mu\text{mol mol}^{-1}$ . (a) diagram of preparation of sample gas mixtures **1**, **2**, **3**, and **4**, (b) diagram of preparation of sample gas mixtures **5**, **6**, **7**, and **8**.

*Preparation of high precision gas mixture of methane, propane, and helium (1):* An evacuated cylinder was weighed and transferred to a filling room. The cylinder was connected to a filling apparatus and propane (30.936 g) was filled into the cylinder. The cylinder was transferred again to the filling room and connected to the filling apparatus. Methane (10.533 g) was filled into the cylinder. The cylinder was transferred a third time to the filling room and connected to the filling apparatus. Helium as dilution gas (104.118 g) was filled into the cylinder. Standard uncertainties of the masses of propane, methane, and helium were 5.4 mg, 5.0 mg, and 5.6 mg, respectively. The concentration of methane in gas mixture **1** and its standard uncertainty were 23989  $\mu\text{mol mol}^{-1}$  and 11  $\mu\text{mol mol}^{-1}$ , respectively. The concentration of propane and its standard uncertainty were 25632  $\mu\text{mol mol}^{-1}$  and 5  $\mu\text{mol mol}^{-1}$ , respectively.

*Preparation of high precision gas mixture of methane, propane, and helium (2):* Gas mixture **1** was used as the starting gas. An evacuated cylinder was weighed, transferred to the filling room, connected to the filling apparatus, and gas mixture **1** (20.778 g) was filled into the cylinder. The cylinder was again transferred to the filling room and connected to the filling apparatus. Helium as dilution gas (116.195 g) was filled into the cylinder. Standard uncertainties of the masses of the starting gas and helium were 4.2 mg and 6.0 mg, respectively. The concentration of methane in gas mixture **2** and its standard uncertainty were 2845.3  $\mu\text{mol mol}^{-1}$  and 1.5  $\mu\text{mol mol}^{-1}$ , respectively. The concentration of propane and its standard uncertainty were 3040.5  $\mu\text{mol mol}^{-1}$  and 0.8  $\mu\text{mol mol}^{-1}$ , respectively.

*Preparation of high precision gas mixture of methane, carbon monoxide, carbon dioxide, and nitrogen (8):* An evacuated cylinder was weighed and transferred to a filling room. The cylinder was connected to a filling apparatus, and gas mixture **5** (10.880 g) was filled into the cylinder. The cylinder was transferred to the filling room again and connected to the filling apparatus. Gas mixture **7** (26.095 g) was filled into the cylinder. The cylinder was transferred to the filling room a third time and connected to the filling apparatus. Gas mixture **6** (50.613 g) was filled into the cylinder. The cylinder was transferred to the filling room a final time and connected to the filling apparatus. Nitrogen as dilution gas (943.534 g) was filled into the cylinder. Standard uncertainties of the masses of methane, carbon monoxide, carbon dioxide, and nitrogen were 4.5 mg, 4.6 mg, 4.4 mg, and 4.5 mg, respectively. The concentration of methane in gas mixture **8** and its standard uncertainty were 1066.7  $\mu\text{mol mol}^{-1}$  and 0.5  $\mu\text{mol mol}^{-1}$ , respectively. The concentration of carbon monoxide and its standard uncertainty were 991.3  $\mu\text{mol mol}^{-1}$  and 0.6  $\mu\text{mol mol}^{-1}$ , respectively. The concentration of carbon dioxide and its standard uncertainty were 1512.6  $\mu\text{mol mol}^{-1}$  and 0.3  $\mu\text{mol mol}^{-1}$ , respectively.

*Preparation of high precision samples solution using gravimetric method*

*n*-Eicosane (178.31 mg) was added to a 30-mL vial, and then *n*-hexadecane (174.34 mg), *n*-dodecane (175.25 mg), and ethylbenzene (168.86 mg) were added. After the addition, the mixture was diluted with acetone (7.5495 g). A portion of the acetone solution (0.3885 g) was further diluted with acetone (6.0711 g), and this final solution was used as the sample. The concentration of ethylbenzene in the sample solution and its standard uncertainty were 673.08  $\mu\text{mol mol}^{-1}$  and 0.26  $\mu\text{mol mol}^{-1}$ , respectively. The concentration of *n*-dodecane and its standard uncertainty were 436.53  $\mu\text{mol mol}^{-1}$  and 0.17  $\mu\text{mol mol}^{-1}$ , respectively. The concentration of *n*-hexadecane and its standard uncertainty were 324.23  $\mu\text{mol mol}^{-1}$  and 0.13  $\mu\text{mol mol}^{-1}$ , respectively. The concentration of *n*-eicosane and its standard uncertainty were 267.54  $\mu\text{mol mol}^{-1}$  and 0.10  $\mu\text{mol mol}^{-1}$ , respectively.

## Results and discussion

The efficiencies of the oxidation and reduction reactions were estimated and the reaction conditions were optimized. Error in the oxidation process due to incomplete reaction was 0.02% at most. Error in the reduction process due to incomplete reaction was sufficiently lower than the uncertainty in the reproducibility of the GC/FID measurement. The final system was then tested on the quantitative analysis of several compounds.

### Optimization of oxidation conditions

Sample responses on the FID with the oxidation micro-reactor were compared to responses where the oxidation micro-reactor was bypassed. In this comparison, the hydrogen reducing reagent was added just before the second micro-reactor with the flow rate fixed at 5 mL min<sup>-1</sup>, bypassing the second micro-reactor. It was found that the oxidation performance was strongly affected by the operation temperature and the flow rate of the oxidizing agent, air.

At first, the influence of reaction temperature on the efficiency of the oxidation was studied. In this study, sample gas mixture **2** was used. Since methane is the most stable species in hydrocarbon compounds for oxidation, it was used to evaluate the oxidation efficiency. Methane in the sample gases was oxidized in the first micro-reactor and converted to carbon dioxide that is not detected by the FID. The efficiency of the oxidation was obtained from the difference between the responses with and without the oxidation micro-reactor. The air flow rate was fixed at 1 mL min<sup>-1</sup>. The reaction efficiency was evaluated at various temperatures between 180 °C to 395 °C and determined to be 99.99% when the reaction temperature was 355 °C or higher. Therefore, as the result of these temperature studies, the oxidation temperature was set to 390 °C.

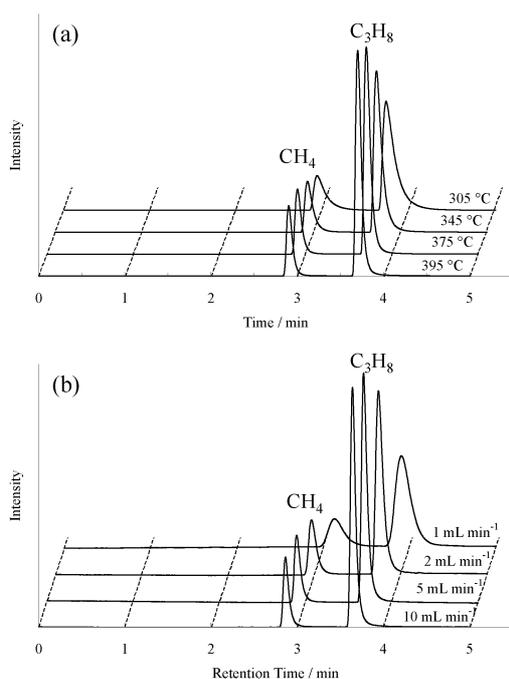
Second, the influence of the air flow rate on the efficiency of the oxidation was studied using sample gas mixtures **1**, **2**, and **3** via

the method described above. Injected amounts of methane in the sample gas mixtures **1**, **2**, and **3** were 98 nmol, 12 nmol, and 1.9 nmol, respectively at 100  $\mu\text{L}$  injected sample. The reaction temperature was set to 390  $^{\circ}\text{C}$ . The reaction efficiency was evaluated with various flow rates between 1  $\text{mL min}^{-1}$  to 10  $\text{mL min}^{-1}$ . The oxidation of methane in the sample gas mixtures proceeded almost completely (99.98%) over the entire range of flow rates studied. Therefore, as the result of these flow rate studies, the air flow rate was set to 1  $\text{mL min}^{-1}$ . Higher concentration of the methane showed leading peak, thus, we decided to use these conditions.

#### Optimization of reduction conditions

Carbon dioxide, which was produced from methane on the oxidizing micro-reactor, was reduced and converted to methane in the second micro-reactor. The peak area of each component in the sample gas mixture was compared with and without the post-column reactions. In this comparison, oxidizing and reducing reagents were added in the same amount.

The influence of reaction temperature on the efficiency of the



**Figure 3.** Chromatograms of methane and propane obtained for the gas mixtures undergoing both oxidation and reduction reactions. The oxidizing reaction temperature was set to 390  $^{\circ}\text{C}$ , and the air flow rate was set to 1  $\text{mL min}^{-1}$ . (a) The reduction was carried out at various reaction temperatures. The sample was gas mixture **2**. The hydrogen flow rate was fixed at 5  $\text{mL min}^{-1}$ . The chromatogram peaks shifted and began to tail at low reaction temperatures. (b) The hydrogen flow rate was varied. The sample was gas mixture **4**. The reduction temperature was fixed at 395  $^{\circ}\text{C}$ . The chromatogram peaks shifted and began to tail at low hydrogen flow rates.

reduction was optimized using gas mixtures **1**, **2**, **3**, and **4**. Injected amounts of methane in the sample gas mixtures **1**, **2**, **3**, and **4** were 98 nmol, 12 nmol, 1.9 nmol and 0.3 nmol, respectively. The hydrogen flow rate was fixed at 5  $\text{mL min}^{-1}$ . Gas mixtures **2**, **3**, and **4** yielded good results, however, the concentration of gas mixture **1** was too high to study. The result of the gas mixture **2** using as sample was shown in Figure 3 a. Although tailing peaks in the chromatograms were observed at lower reaction temperatures, the reduction proceeded completely at temperatures between 305  $^{\circ}\text{C}$  and 395  $^{\circ}\text{C}$ . Adsorptions on the catalyst in the reactor and on the inner surface of the reactor could have been factors which caused the tailing peaks. Therefore, as a result of these temperature studies, the reduction temperature was set to 395  $^{\circ}\text{C}$ .

The effect of the hydrogen flow rate was measured using gas mixtures **2**, **3**, and **4** and showed similar results. The result of the sample gas mixture **4** was shown in Figure 3 b. The hydrogen flow rate at 1  $\text{mL min}^{-1}$  (5 times amount of added oxygen) was enough to reduce the oxidized sample completely. However, peak broadening was observed in the micro-reactor at low flow rates. Therefore, the flow rate of hydrogen was fixed at 5  $\text{mL min}^{-1}$  (25 times amount of added oxygen).

#### Application to Carbon Monoxide and Carbon Dioxide

Quantitative analysis of carbon monoxide and carbon dioxide was carried out using our system. Gas mixture **8** was used which contained methane, carbon monoxide, and carbon dioxide. Methane in this sample gas was used as the internal standard. The analyte concentrations were calculated with Eq. (1),

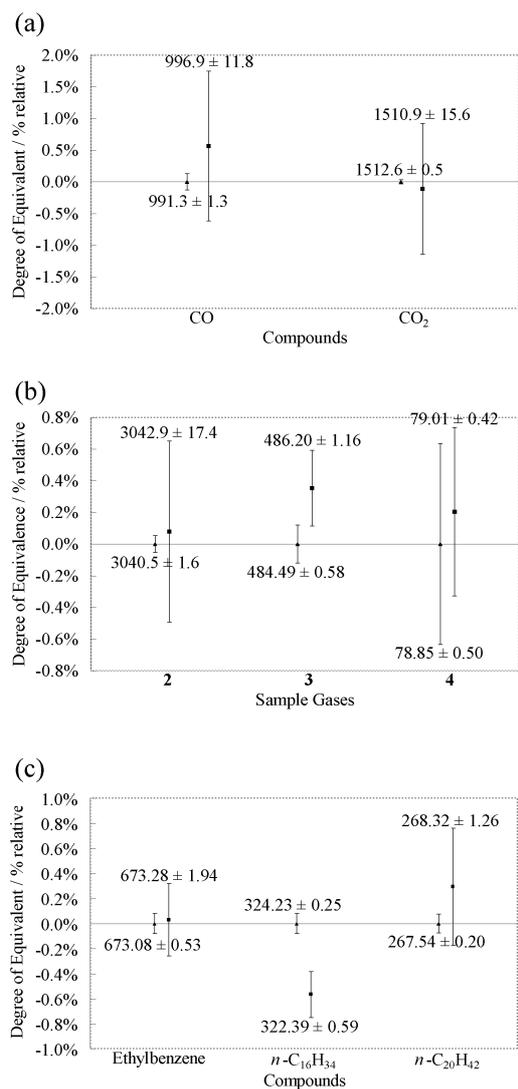
$$C_x = \frac{A_x}{A_{std}} \times C_{std} \times \frac{K_{std}}{K_x} = A'_x \times C_{std} \times \frac{K_{std}}{K_x} \quad (1)$$

where  $C_x$  was the analyte concentration in the sample ( $\text{mol mol}^{-1}$ ),  $C_{std}$  was the concentration of the standard material ( $\text{mol mol}^{-1}$ ),  $A_x$  was the obtained peak area of the sample,  $A_{std}$  was the obtained peak area of the standard material,  $K_x$  was the carbon number of the sample, and  $K_{std}$  was the carbon number of the standard material. The term  $A'_x$  was the peak area ratio of  $A_{std}$  and  $A_x$ . The combined uncertainty was calculated by using the Eq. (2),

$$u_c = \sqrt{u_{rep}^2 + u_{std}^2} \quad (2)$$

where  $u_c$  was the combined standard uncertainty,  $u_{rep}$  was the standard deviation of the peak ratio, and  $u_{std}$  was the standard uncertainty of the standard material. Expanded uncertainty<sup>15</sup> of the analyte concentration was the product of the  $u_c$  and coverage factor<sup>15</sup>  $k$ .

The analytical results of carbon monoxide and carbon dioxide for ten measurements were summarized in Figure 4 a. The vertical axis of the figure means the relative difference of the reference values and the obtained values. The relative error of the obtained analytical results with the post-column reaction GC/FID system was below 1%. This result was in good agreement with the reference



**Figure 4.** Comparison of the reference values of target compounds' concentrations in sample mixture with the results obtained by the post-column reaction GC/FID. Units of the values (mean  $\pm$  expanded uncertainty,  $k=2$ ) of the reference and the result were  $\mu\text{mol mol}^{-1}$ . (a) Gas mixture **8** was used. Target compounds were carbon monoxide and carbon dioxide.  $\square$ : reference value of each target compounds;  $\bullet$ : obtained result. (b) Gas mixtures **2**, **3**, and **4** were used. Target compound was propane.  $\square$ : reference value of each sample gas mixture;  $\bullet$ : obtained result. (c) Liquid sample was used. Target compounds were ethylbenzene, *n*-hexadecane, and *n*-eicosane.  $\square$ : reference value of each sample gas mixture;  $\bullet$ : obtained result.

values. The result showed that one component, methane, was used as the internal calibration component and the others, carbon monoxide and carbon dioxide, were able to be calibrated precisely. Thus, this post-column reaction GC/FID system is acceptable to use as a primary ratio method. All components of tested gas mixture showed same response, and then oxidation/reduction per-

formed perfect in this system, too.

#### Application to Nonmethane Hydrocarbons

Quantitative analysis of propane using methane as the calibration standard was carried out with our system. Gas mixtures **2**, **3**, and **4** were used which contained both methane and propane. Methane in the sample gas was used as an internal standard. The propane concentration and its combined uncertainty were calculated by using Eqs. (1) and (2). Three measurements for each sample mixture were obtained, and the analytical results are summarized in Figure 4 b. The relative error of the obtained analytical results with the post-column reaction GC/FID system was below 1%. The analytical values were in agreement with reference values. Under the same conditions as those in Table 1, the relative responses per carbon atom for methane to propane, of the sample gas mixture **2**, **3**, and **4** were summarized in Table 4.

This technique can also be applied to liquid samples. Quantitative analysis of an acetone solution of ethylbenzene, *n*-hexadecane, and *n*-eicosane, using *n*-dodecane as an internal calibration standard, was carried out. Injected carbon molecules of ethylbenzene, *n*-dodecane, *n*-hexadecane, and *n*-eicosane in the sample solution were 7.3 nmol, 7.1 nmol, 7.1 nmol and 7.3 nmol, respectively. The method of calculating the concentrations and uncertainties of the target three compounds was the same method as the calculation method for the propane concentration and its combined uncertainty. Ten measurements were obtained, and the analytical results are summarized in Figure 4 c. The analytical results, except for that of *n*-hexadecane, were in good agreement with the prepared values. Although the result for *n*-hexadecane was slightly lower than the prepared values, the difference between the obtained result and the prepared values was only  $1.84 \mu\text{mol mol}^{-1}$ . This difference was equivalent to 0.57% of the prepared value; however, it is not an abnormal situation that the error acquired using a normal GC/FID is 0.57%. Therefore, the obtained results were in agreement with reference values. Under the same conditions as those in Table 2, the results of the relative responses for ethylbenzene, *n*-hexadecane, *n*-eicosane to *n*-dodecane were summarized in Table 4.

These results demonstrate that this post-column reaction GC/FID system is acceptable to use as a primary ratio method, and this system is a useful method for the precise quantitative analysis of hydrocarbons.

#### Conclusion

A post-column reaction GC/FID system was developed and the efficiencies of the reactions were evaluated. Reaction efficiencies of the two micro-reactors were good, and the reactions went nearly to completion. The tested compounds were converted into methane by passing through the post-column reactors and then de-

Table 4. Relative response on FID for target hydrocarbons to the reference compounds per carbon atom with/without using the post-column reactors

Compounds		Sample	Relative response for the target compound to the reference compound per carbon atom	
Target	Reference		Without	With
Methane	Propane	2	1.050 ± 0.002	0.999 ± 0.003
Methane	Propane	3	–	0.996 ± 0.001
Methane	Propane	4	–	0.998 ± 0.002
Ethylbenzene	<i>n</i> -Dodecane	8	0.982 ± 0.001	1.000 ± 0.001
<i>n</i> -Hexadecane	<i>n</i> -Dodecane	8	1.005 ± 0.002	0.994 ± 0.001
<i>n</i> -Eicosane	<i>n</i> -Dodecane	8	1.008 ± 0.003	1.002 ± 0.001

tected as methane. Quantitative analysis was carried out using the developed system, and the relative error of the obtained analytical results with the post-column reaction GC/FID system was below 1%. Although this post-column GC/FID system was more complex than the conventional response factor method, uncertainty of the analysis was much less than the response factor method. Furthermore, in this system, only one standard material was required and the cost for analysis was greatly reduced compared to the conventional calibration method using calibration standards for each analyte. This post-column reaction GC/FID system can be applied to precise quantitative analysis using any of the compounds in the sample as the internal calibration standard. These results also indicated the post-column reaction GC/FID system is acceptable to use as a primary ratio method. This method is expected to expand other compounds which produce carbon dioxide and/or carbon monoxide by oxidation, e.g., alkenes, alkynes, alcohols, ethers, esters, etc. Results of these studies will be reported in the near future.

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