SHIMADZU
Excellence in Science

LAAN-B-GC004

Tracera (GC-BID) Solution

Highly Versatile GC Analyzer for Trace Analysis

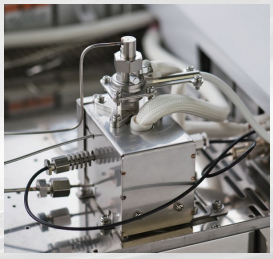
Tracera

The new Tracera GC System is now ready to solve your trace analysis needs. This system utilizes the new Barrier Discharge Ionization Detector technology coupled with a GC-2010 Plus capillary gas chromatograph to create a GC system that makes it possible to reveal trace components that are difficult to see by other GC detectors.

The New Detector BID-2010 Plus

BID-2010 Plus is a completely new universal detector and a highly sensitive device that creates inization from a Helium-based, dielectric barrier discharge plasma.

Cover part of BID-2010 Plus

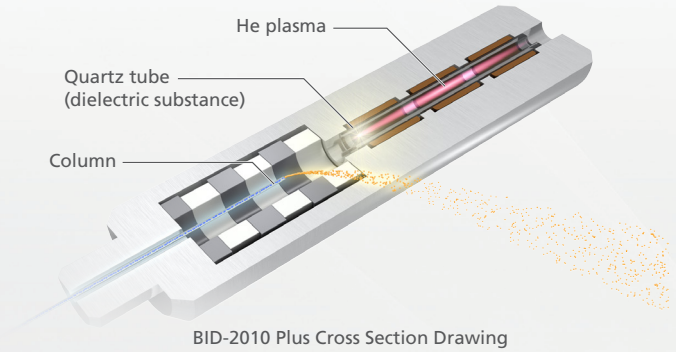


Main body of BID-2010 Plus

Contents

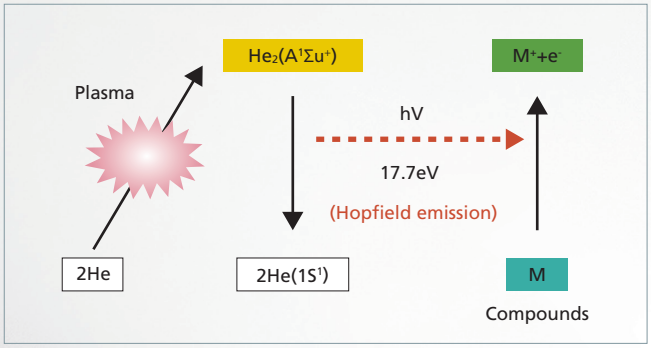
Introduction of Tracera	2
Applications	
Improvement of Sensitivity and Repeatability in Analysis of Formic Acid	6
High-Sensitivity Analysis of Formic Acid in Artificial Photosynthesis Research	8
Determination of Trace Formic Acid in Industrial Acetic Acid	10
Analysis of Reaction Products in Artificial Photosynthesis Research	12
High-Sensitivity Simultaneous Analysis of Inorganic Gases and Light Hydrocarbons	13
High-Sensitivity Analysis of Impurities in Gas	14
Trace Analysis of Carbon Dioxide in High-Purity Hydrofluorocarbon	15
Simultaneous Analysis of Evolved Gas Produced by the Degradation of a Lithium-Ion Battery	16
Analysis of Permanent Gases Using Customized GC	18
Ultrafast Analysis of Natural Gas Using Customized GC	20
Ultrafast Analysis of Refinery Gas Using Customized GC	22
Analysis of Extended Refinery Gas Using Customized GC	25

BID-2010 Plus Principals for Detection



BID-2010 Plus Cross Section Drawing

A plasma is generated by applying a high voltage to a quartz dielectric chamber, in the presence of helium. Compounds that elute from the GC column are ionized by this He plasma, then captured with collection electrodes and described as peaks.



Principal of Ionization Reaction

	Ionization Energy (eV)
Ne	21.6
N_2	15.6
H_2	15.4
CO	14.0
CO_2	13.8
CH_4	12.5
O_2	12.1
MeOH	10.9
Hexane	10.2
Acetone	9.7
Benzene	9.3

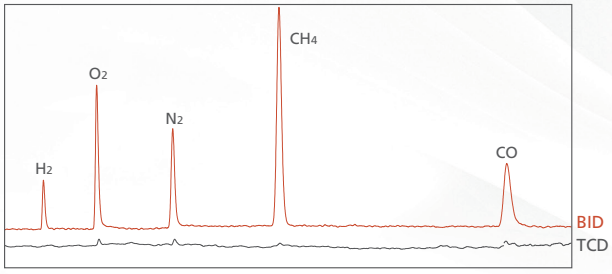
The photon energy of He is extremely high (17.7 electron volt). Therefore it makes possible to detect every compound except Ne (neon) and He which is the plasma gas, with high sensitivity. The BID is truly the universal plasma detector for next generation.

*The BID was developed thru collaborative research with Dr. Katsuhisa Kitano, Center for Atomic and Molecular Technologies, Graduate School of Engineering, Osaka University.

Features of BID-2010 Plus

1) Over 100x Higher Detection Sensitivity than TCDs — Effective Trace Impurity Analysis

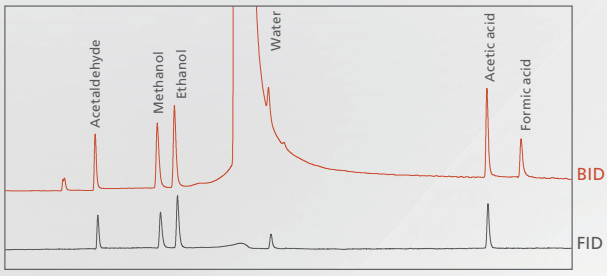
The barrier discharge ionization detector (BID) offers highly sensitive detection of all components except He and Ne (over 2 times higher sensitivity than FIDs and over 100 times higher than TCDs). In inorganic gas analysis or analysis of mixtures of inorganic and organic compounds, the BID can detect trace components at the ppm level, which cannot be achieved by TCDs.



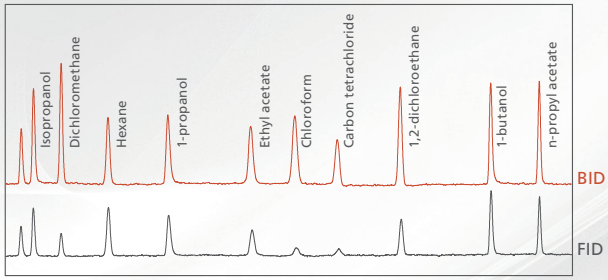
10 ppm concentration each component in He,
1:30 split analysis, 0.5 mL sample volume

2) Detection of Compounds to Which FIDs Offer Low Sensitivity

The FID tends to achieve lower sensitivity for compounds containing the hydroxyl group (-OH), aldehyde group (-CHO), or halogens (fluorine (F), chlorine (Cl), etc.) than for other hydrocarbon compounds. Therefore, the FID offers low analysis sensitivity to aldehydes, alcohols, and halides. In contrast, the BID achieves superior analysis sensitivity to such compounds, with less difference in relative response between compounds.



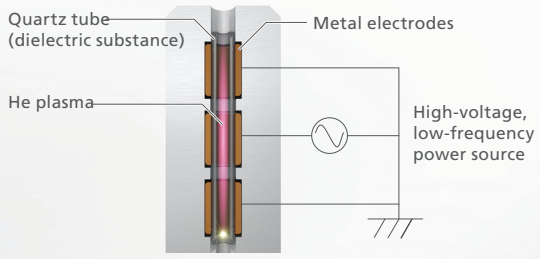
100 ppm concentration each component in water,
1:24 split analysis, 0.5 µL sample volume



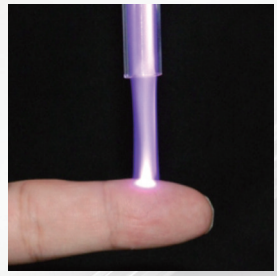
10 ppm concentration each component in MeOH,
1:29 split analysis, 1µL sample volume

3) Stable Analysis for a Long Period of Time

The barrier discharge technology used on the BID offers a structure where plasma does not make any contact with electrodes. Since the temperature of plasma is close to room temperature, the BID electrodes do not become too hot. Therefore, the electrodes practically never deteriorate, enabling stable analysis for a long period of time.



Cross Section Drawing of BID-2010 Plus



Low-temperature plasma

4) Safe Flameless Detector

The BID uses only helium as the detector gas. Unlike FIDs, it requires no hydrogen flame. The BID can be used with confidence in laboratories where use of FIDs is restricted. Its maximum 350 °C operating temperature supports the analysis of high-boiling-point liquid samples in addition to gas samples.

Improvement of Sensitivity and Repeatability in Analysis of Formic Acid

In the study of artificial photosynthesis and impurity analysis of raw materials and chemical products, high-sensitivity analysis of formic acid has become an important requirement. When conducting analysis of formic acid by gas chromatography (GC), detection is typically conducted using either a thermal conductivity detector (TCD) or a combination of methanizer + FID detector. As the TCD is appropriate for relatively low-sensitivity detection, it is mainly used for analysis of high-concentration samples, while the methanizer + FID combination is used in analysis of low-concentration samples. Because the FID alone exhibits little or no response to formic acid as is, it must first be reduced to methane using a methanizer, which then permits detection by FID. A methanizer can be a useful tool, but it does have its disadvantages under certain conditions, including deactivation of the catalyst if the oxygen concentration in the sample is greater than 100 ppm, or if the sample environment is high in carbon dioxide. Furthermore, if excessive water enters the system, it can take considerable time to restore the system. These disadvantages require the use of a valve system to eliminate oxygen or carbon dioxide. On the other hand, a barrier discharge ionization detector (BID) is a detector that is capable of detecting formic acid at ppm-order concentrations, thereby permitting high-sensitivity measurement, as long as coexisting components such as oxygen can be separated by the column.
In this section, an example of high sensitivity analysis of formic acid included in various organic solvents using Tracera is reported.

1. Experiments

1.1 Apparatus

Software	GCsolution
Gas chromatograph	Tracera (GC-2010 Plus A + BID-2010 Plus)

1.2 Conditions of Analysis

Column	Rtx-WAX, 60 m × 0.53 mm × 1.0 µm
Column temperature program	80 °C – 5 °C/min – 130 °C – 15 °C/min – 230 °C (3 min)
Carrier gas	He
Carrier gas control mode	Linear Velocity Mode (50 cm/sec)
Injection mode	Split (2:1)
Injection port temperature	240 °C
Detector temperature	240 °C
Discharge gas flow	He: 50 mL/min
Injection volume	1.0 µL
Glass Insert	RESTEK Sky Inlet Liner P/N 23319.1

2. Results and Discussion

2.1 Validation of Phosphoric Acid Treatment

When conducting GC measurement of formic acid at low concentrations, care must be taken to prevent adsorption to the various component surfaces. To prevent adsorption at the injection port, phosphoric acid treatment of the glass insert is essential. Here, after immersing the wool-filled glass insert (Restek Sky Inlet Liner, P/N: 23319.1) in 0.3 % phosphoric acid / acetone solution for one minute, it was removed, dried and then used for the analysis. Fig. 1 shows the pretreatment procedure flow used for the glass insert, and Fig. 2 shows the effectiveness of this pretreatment in low-concentration analysis. When measurement of a 10-ppm (v/v) formic acid solution (solvent: acetone) was conducted using the analytical conditions shown in 1.2 Conditions of Analysis, peak detection was not achieved using an untreated glass insert, while detection with good sensitivity was achieved using a glass insert that had been pretreated with phosphoric acid. The following analyses were conducted using the analytical conditions shown in 1.2 Conditions of Analysis.

Position of wool packing is adjusted so that its upper edge is 25 mm from top of insert.
↓
Prepare 0.3 % phosphoric acid / acetone solution.
↓
Immerse wool-packed insert in 0.3 % phosphoric acid / acetone solution for 1 minute.
↓
Remove, and then dry with air or nitrogen gas streams.

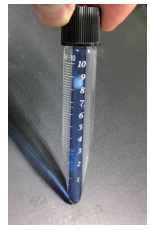


Fig. 1 Glass Insert Phosphoric Acid Treatment Procedure

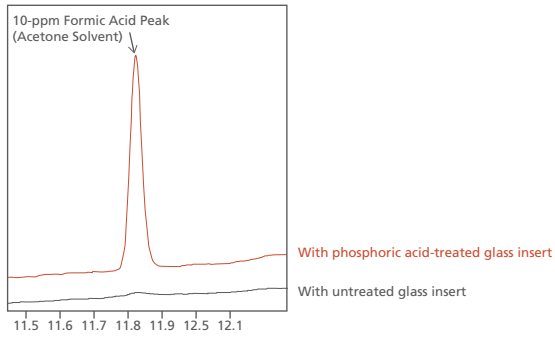


Fig. 2 Effectiveness of Glass Insert Phosphoric Acid Treatment in Low-Concentration Formic Acid Analysis

The Rtx-WAX column (Restek Co.) was used for the analysis. Peak tailing was evident when measurement of a 10-ppm (v/v) formic acid aqueous solution (Solvent: Acetone) was conducted using an unused column directly after aging treatment. We then applied the same phosphoric acid treatment that was used for the glass insert to the column as well. The column phosphoric acid treatment procedure is shown in Fig. 3. A 100-ppm (v/v) phosphoric acid / methanol solution was measured four times, and this was followed by ten repeat measurements methanol alone using a constant column temperature of 150 °C (the other conditions were the same as those shown in 1.2 Conditions of Analysis. Then, we conducted repeat measurements of 10-ppm (v/v) formic acid solution (Solvent: Acetone), and we checked the stability of the peak shape and retention time. A comparison of the peak shapes of formic acid before and after the column phosphoric acid treatment is shown in Fig. 4. The comparative results confirmed that the peak shape was sharper following phosphoric acid treatment of the column.

Prepare 100-ppm phosphoric acid / methanol solution.
↓
Conduct four repeat measurements using conditions of Table 1.
↓
Stabilize column using ten repeat measurements of methanol with column at 150 °C (other conditions the same as shown in Table 1).
↓
Check repeatability of peak shape and retention time by repeat measurement of 10-ppm formic acid / acetone solution.

Fig. 3 Procedure for Column Phosphoric Acid Treatment

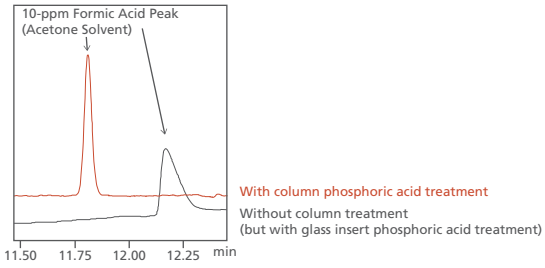


Fig. 4 Comparison of Formic Acid Peak Shapes Before and After Column Phosphoric Acid Treatment

To check the stability obtained with the glass insert and column phosphoric acid treatment, 100 repeat measurements of a 10-ppm (v/v) formic acid solution (Solvent: Acetone) were conducted. The area repeatability obtained was CV 1.6 %, and considering that the septum replacement guideline is based on 100 analyses, this confirms the effectiveness of the phosphoric acid treatment (Fig. 5). Although the Rtx-WAX column was used in this study, we have not yet evaluated whether or not the same results would be obtained with other WAX columns. Further, since a column subjected to the same phosphoric acid treatment may have an adverse effect when used to conduct a different analysis, it is advisable to use the column specifically for formic acid analysis.

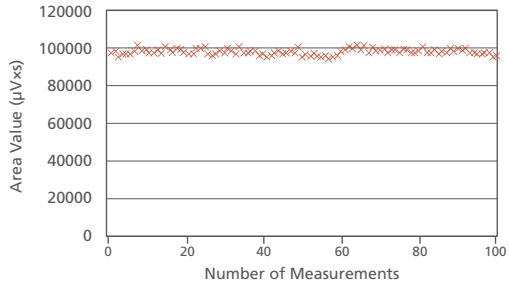


Fig. 5 Repeatability of Peak Area with 10-ppm Formic Acid / Acetone Solution at the Hundredth Analysis

2.2 Analysis of Low-Concentration Formic Acid in Various Organic Solvents

We checked the linearity of results using various concentrations of formic acid (1, 10, 50 ppm (v/v)) in different solvents, including acetone, *N,N*-dimethylacetamide, acetonitrile, and methanol. The linearity and chromatograms obtained in analysis of the acetone, *N,N*-dimethylacetamide, acetonitrile, and methanol solvent samples are shown in Figs. 6 to 9, respectively.

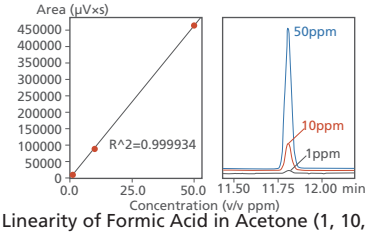


Fig. 6 Linearity of Formic Acid in Acetone (1, 10, 50 ppm)

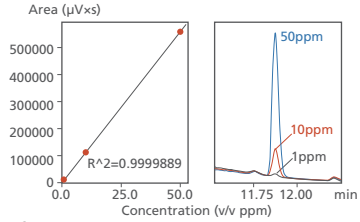


Fig. 7 Linearity of Formic Acid in *N,N*-Dimethylacetamide (1, 10, 50 ppm)

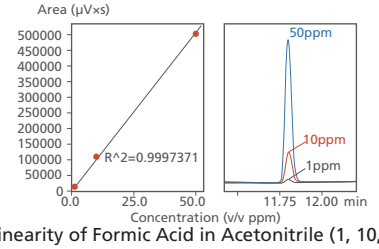


Fig. 8 Linearity of Formic Acid in Acetonitrile (1, 10, 50 ppm)

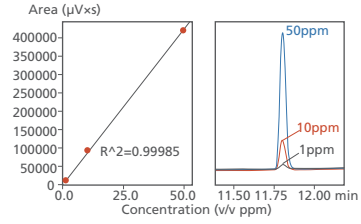


Fig. 9 Linearity of Formic Acid in Methanol (1, 10, 50 ppm)

High-Sensitivity Analysis of Formic Acid in Artificial Photosynthesis Research

Artificial photosynthesis refers to a technique of creating high-energy materials using photocatalysis and solar energy, and is expected to play a role in the development of next-generation renewable energy. In the photochemical carbon dioxide reduction reaction, which is currently a research theme, there are instances in which formic acid is the main reaction product. Analysis of formic acid is typically conducted by liquid chromatography, ion chromatography or capillary electrophoresis, etc. However, since analysis of the formic acid dissolved in the organic solvent requires at least a ten-fold dilution of the solvent using water or mobile phase, such a low-concentration analysis can sometimes be difficult. On the other hand, since a gas chromatograph (GC) can directly measure organic solvents as is without dilution, use of the BID-2010 Plus for high-sensitivity detection of formic acid permits analysis at the ppm level.
In this section, we introduce an example in which the GC-BID is used for analysis of formic acid in an actual sample consisting of the solvent *N,N* -dimethylacetamide, used in the research of artificial photosynthesis. Also, regarding analysis of formic acid at low concentrations, additional cautionary notes can be found in previous application "Improvement of Sensitivity and Repeatability in Analysis of Formic Acid".

1. Experiments

1.1 Apparatus

Software	GCsolution
Gas chromatograph	Tracera (GC-2010 Plus A + BID-2010 Plus)

1.2 Conditions of Analysis

Column	Rtx-WAX, 60 m × 0.53 mm × 1.0 µm
Column temperature program	80 °C – 5 °C/min – 130 °C – 15 °C/min – 230 °C (3 min)
Carrier gas	He
Carrier gas control mode	Linear Velocity Mode (50 cm/sec)
Injection mode	Split (2:1)
Injection port temperature	240 °C
Detector temperature	240 °C
Discharge gas flow	He: 50 mL/min
Injection volume	1.0 µL
Glass Insert	RESTEK Sky Inlet Liner P/N 23319.1

2. Results and Discussion

2.1 Analysis of Actual Sample Obtained from Artificial Photosynthesis Reaction

The sample solution consisted of the solvent *N,N* -dimethylacetamide used for carbon dioxide reduction reaction, in which 0.1 M tetraethylammonium tetrafluoroborate (NEt_4BF_4) was dissolved[1)]. The analytical conditions used are shown in 1.2 Conditions of Analysis. The sample solution was spiked with formic acid at 10 ppm (v/v), and ten repeat measurements were then conducted. The formic acid peak areas showed a gradual decline, as can be seen in Fig. 1.

1) This sample was provided by Professor Osamu Ishitani of the University of Tokyo Institute of Technology, Graduate School of Science and Engineering.

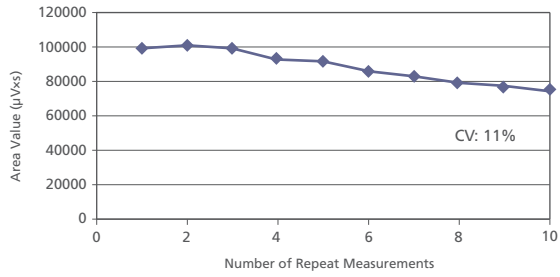


Fig. 1 Changes in Formic Acid Peak Area before Pretreatment

Since it was presumed that the adsorption of formic acid in the GC injection unit was due to accumulation of the electrolyte NEt_4BF_4 which coexists with the sample in the injection unit, the NEt_4BF_4 was removed prior to GC measurement using a cation exchange cartridge (Alltech Maxi-Clean 0.5 mL IC-H 50 pk, P/N 30264). The NEt_4BF_4 removal procedure is shown in Fig. 2. We then conducted ten repeat measurements of the sample after eliminating the NEt_4BF_4, and verified results with good repeatability (Fig. 3). It is believed that the influence of salt was removed by replacing the cation (NEt_4^+) with H^+ using a cation exchange cartridge.

Cartridge conditioning DMA 5 mL, at 2 mL/min

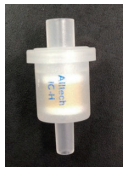
↓

Sample flow-through

3mL (disposal of 2 mL, recovery of 1 mL), 1 mL/min or less

↓

GC Analysis



Alltech Maxi-Clean 0.5 mL IC-H 50 pk
PN: 30264
Strong cation exchange
If the salt of monovalent ion is contained 0.1 M in a sample, about 9 mL of sample can be processed.

Fig. 2 Pretreatment Procedure Using Cation-Exchange Cartridge

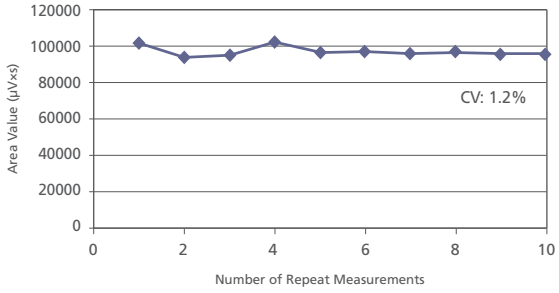


Fig. 3 Changes in Formic Acid Peak Area after Pretreatment

To verify the rate of recovery, sample solutions spiked with formic acid at 1, 10 and 50 ppm (v/v), respectively, were subjected to pretreatment according to the procedure of Fig. 2, and then measured by GC. The results are shown in Table 1. The rates of recovery were nearly 100 %. Further, to check the repeatability of the pretreatment procedure, a sample solution spiked with 10 ppm (v/v) formic acid was subjected to pretreatment and measurement five times, once each per sample. The chromatogram is shown in Fig. 4, and the formic acid peak area repeatability values are shown in Table 2.

Table 1 Results of Recovery Test

	Quantitation Value ppm (n=3 mean)
Spiked at 1 ppm	0.97
Spiked at 10 ppm	9.5
Spiked at 50 ppm	50

Table 2 Results of Pretreatment Repeatability Test

Formic acid peak area	1st	2nd	3rd	4th	5th	Mean	SD	RSD%
	97159	94176	91712	92819	91562	93485.6	2305.47	2.47

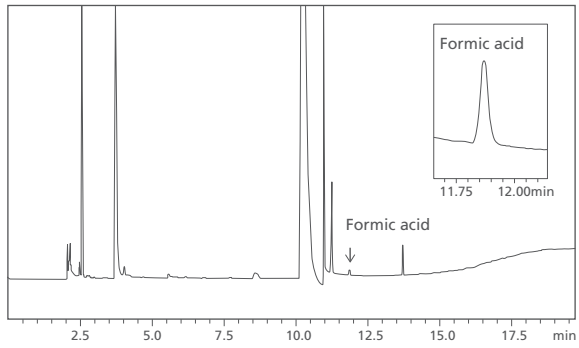


Fig. 4 Chromatogram from Analysis of 10 ppm Pretreated Formic Acid in Actual Sample Solution

Determination of Trace Formic Acid in Industrial Acetic Acid

A method for determination of formic acid in industrial acetic acid using Tracera is reported here. The method has good linearity in the concentration range of 0.001 % to 0.5 % with a correlation coefficient greater than 0.999. A repeatability test was carried out on 6 repeated injections of 0.01 % formic acid standard solution and the RSD% of peak area was lower than 2 %, suggesting good peak area repeatability. The method can be used for fast quantitative determination of trace formic acid in industrial acetic acid.

With the price of crude oil soaring and the predicted shortage of petroleum and natural gas resources in the future, the world has become more and more dependent on the development of the coal chemical industry.

Acetic acid is an important raw material in coal-based chemical synthesis that can be used for the production of polyethylene, cellulose acetate, polyvinyl alcohol, synthetic fibers and textiles. It is expected that there will be extensive demand for acetic acid in the coming years. The estimated production of acetic acid in China in 2010 was 730,000 tons.

The purity of acetic acid contributes to the quality of coal-based synthesized products and formic acid is one of the major impurities in acetic acid. According to literature on the analysis of formic acid in acetic acid by gas chromatography (GC), thermal conductivity detectors (TCD) are the commonly used detectors because of the poor response of flame ionization detectors (FID). For example, a method based on packed column and GC-TCD is proposed in Chinese national standard GB/T 1628-2008 (Glacial acetic acid for industrial use) for the analysis of acetic acid. It is stipulated in the standard that the content of formic acid in premium grade acetic acid shall be less than 0.05 %, but the sensitivity of thermal conductivity detectors (TCD) falls short of this level and may impede the accurate quantitation of formic acid in acetic acid.

Shimadzu has recently released a general-purpose detector, the barrier discharge ionization detector (BID). The BID is the latest generation of general-purpose detector. It uses high purity helium gas for the generation of a helium plasma jet, which produces high photon energy (17.7 eV) and can ionize all types of compounds with the exception of neon and the carrier gas helium. It is 100 times more sensitive than a TCD.

A method is proposed in this paper for the determination of trace formic acid in industrial acetic acid with the Shimadzu BID. With the merits of simple operation, high sensitivity, low LOD, and good adaptability, the method is suitable for the analysis of trace formic acid in industrial acetic acid and beneficial to quality assurance of chemically synthesized products made with acetic acid.

1. Experiments

1.1 Apparatus

Software	GCsolution
Gas chromatograph	Tracera (GC-2010 Plus A + BID-2010 Plus)

1.2 Conditions of Analysis

Column	InertCap WAX, 30 m × 0.25 mm × 0.25 µm
Column temperature program	60 °C (2 min) – 8 °C/min – 150 °C (5 min)
Carrier gas	He
Carrier gas control mode	Linear Velocity Mode (25 cm/sec)
Injection mode	Split (10:1)
Injection port temperature	250 °C
Detector temperature	250 °C
Discharge gas flow	He: 70 mL/min
Injection volume	1.0 µL
Purge flow	5 mL/min

1.3 Pretreatment of samples

A 1.0 µL sample was directly pipetted and injected for analysis without being subjected to any pretreatment.

2. Results and Discussion

2.1 Standard chromatogram

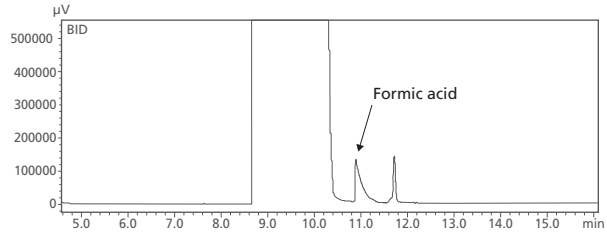


Fig. 1 Chromatogram of Formic Acid Standard Solution (0.05 %)

Table 1 Information and Retention Time of Formic Acid

No.	Name	CAS#	Retention Time (min)
1	Formic acid	64 - 18 - 6	10.740

2.2 Calibration curve and correlation coefficient

A series of acetic acid standard solutions of concentrations of 0.001, 0.005, 0.01, 0.05, 0.1, and 0.5 % were prepared and a calibration curve as shown in Fig. 2 was plotted with concentration as the X-axis and peak area as the Y-axis. The apparatus' LOD was calculated (as 3 times the SNR) based on its response to 0.001 % acetic acid standard solution. The result was as shown in Table 2.

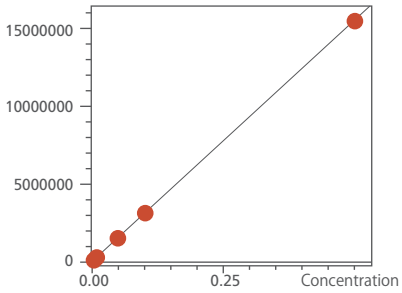


Fig. 2 Calibration Curve of Formic Acid

Table 2 Correlation Coefficient and LOD

No.	Analyte Name	Correlation Coefficient	LOD (%)
1	Formic acid	0.99998	0.00005

2.3 Repeatability

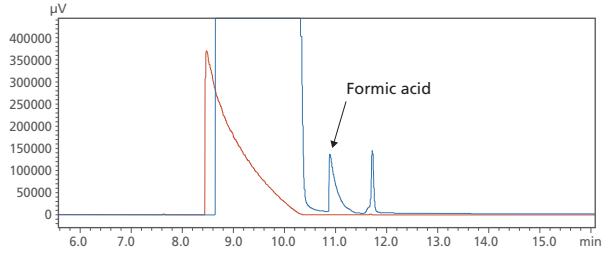
Six repeated injections of 0.01 % standard solution were made and, as shown in Table 3, the assay results suggested that the method has good area repeatability.

Table 3 Peak Area Repeatability of Formic Acid (n=6)

No	Analyte Name	1	2	3	4	5	6	Mean	RSD%
1	Formic acid	352869	363833	367052	364370	367744	370922	364465	1.71

2.4 A Comparison of the Sensitivity of BID and TCD

A 0.05 % formic acid standard solution was subjected to analysis with GC-BID and GC-TCD, respectively, and the detectors were compared in terms of their sensitivity to formic acid. The results were as shown in Fig. 3.



(The blue line corresponds to the assay result with BID and the pink line corresponds to the determination result with TCD.)

Fig. 3 A Sensitivity Comparison of BID and TCD

2.5 Sample Assay Results

An industrial acetic acid sample (1.0 μL) was pipetted and directly injected for analysis, yielding a chromatogram as shown in Fig. 4. The quantitative assay result was as shown in Table 4.

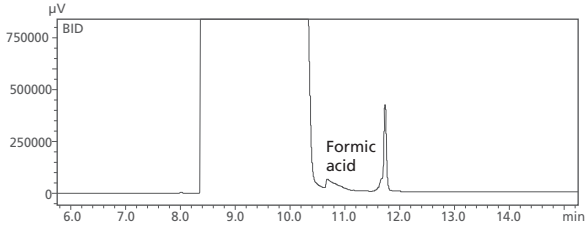


Fig. 4 Chromatogram of an Actual Sample

Table 4 Quantitation Result of an Actual Sample

No.	Analyte Name	Quantitation result (%)
1	Formic acid	0.016

3. Conclusion

A method was proposed for the determination of formic acid in industrial acetic acid using the Shimadzu gas chromatograph and BID-2010 Plus detector. The method has the merits of simple operation, no pretreatment, and high sensitivity and demonstrated good linearity and repeatability in the concentration range of 0.001 to 0.5 %. It is sufficient for the detection and assay of trace formic acid in acetic acid.

Analysis of Reaction Products in Artificial Photosynthesis Research

Artificial photosynthesis refers to a technique for the manufacture of high-energy substances using energy from sunlight. It is expected to become the 4th type of sunlight-based renewable energy after solar cells, solar heating, and biomass technologies.
An example of the simultaneous analysis of CO and H_2, generated in a photochemical carbon dioxide reduction utilizing a photo-catalyst using Tracera is reported here.

1. Experiments

1.1 Apparatus

Software	GCsolution
Gas chromatograph	Tracera (GC-2010 Plus A + BID-2010 Plus)

1.2 Conditions of Analysis

Column	Micropacked ST
Column temperature	35 °C (2.5 min) - 20 °C /min - 180 °C (0.5 min) Total.10.25 min
Carrier gas controller	Pressure
Pressure program	250 kPa (2.5 min) – 15 kPa/min – 360 kPa (0.42 min) (He)
Injection mode	Split (10:1)
Injection port temperature	150 °C
Detector temperature	280 °C
Discharge gas flow	70 mL/min
Injection volume	50 µL

2. Results

Fig. 1 shows a chromatogram of substances generated in a photochemical carbon dioxide reduction. Fig. 2. shows a graph of CO and H_2 production plotted against reaction time. It was confirmed that CO production increased sharply for the first 30 minutes of reaction time, after which it shifted to a more gradual increase.
The BID detector in the Tracera system can provide simultaneous high-sensitivity measurements of CO and H_2. This detector can detect all components eluted from the column, thus enabling acquisition of a variety of information as well as the target component measurements.

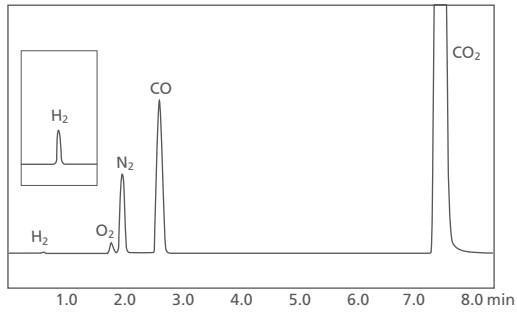


Fig. 1: Chromatogram of Substances Generated in a Photochemical Carbon Dioxide Reduction

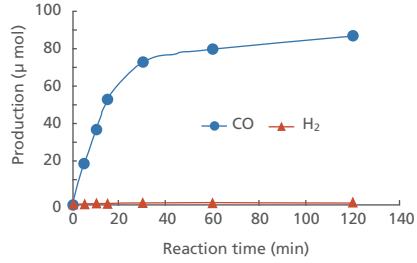


Fig. 2: CO and H_2 Production Versus Reaction Time

Data from Dr. Hitoshi Ishida and Dr. Yusuke Kuramochi, Department of Chemistry, School of Science, Kitasato University;
CREST, Japan Science and Technology Agency

High-Sensitivity Simultaneous Analysis of Inorganic Gases and Light Hydrocarbons

With conventional analytic methods, the high-sensitivity detection of CO, CO_2 and light hydrocarbons requires a Methanizer plus a flame ionization detector (FID), while the detection of inorganic gas components requires a thermal conductivity detector (TCD).
This requires a system with a complicated flow channel configuration. However, if the appropriate analysis column can be selected utilizing a barrier discharge ionization detector (BID) as the detector, then a mixed gas sample containing inorganic gases and light hydrocarbons can be simultaneously analyzed with high sensitivity. In this section, an example of the high-sensitivity simultaneous analysis of inorganic gases and light hydrocarbons using Tracera is reported.

1. Experiments

1.1 Apparatus

Software	GCsolution
Gas chromatograph	Tracera (GC-2010 Plus A + BID-2010 Plus)
Gas sampler	MGS-2010

1.2 Conditions of Analysis

Column	Micropacked ST
Column temperature	35 °C (2.5 min) - 20 °C /min - 250 °C (0 min) - 15 °C /min - 270 °C(5.42 min) Total. 20 min
Carrier gas controller	Pressure
Pressure program	250 kPa(2.5 min) – 15 kPa/min – 400 kPa(7.5 min) (He)
Injection mode	Split (5:1)
Injection port temperature	150 °C
Detector temperature	280 °C
Discharge gas flow	70 mL/min
Injection volume	1.0 mL

2. Results

Fig. 1 shows the chromatogram for a standard gas sample containing inorganic gases and light hydrocarbons (5 ppm each, He balanced). It is evident that a high-sensitivity simultaneous analysis of inorganic gases and light hydrocarbons is possible with a simple instrument configuration.

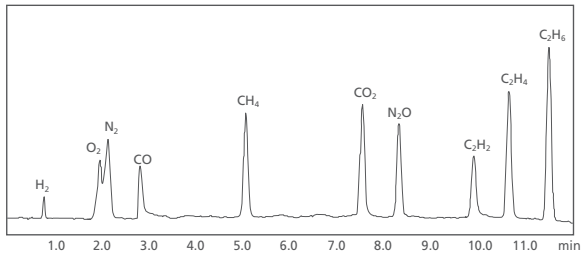


Fig. 1: Chromatogram for 5 ppm Components in He Standard Sample

The inorganic gas and light hydrocarbon standard gas sample (5 ppm each, He balanced) was analyzed successively, and the peak area measurements were repeated to confirm repeatability. The overlapping chromatograms are shown in Fig. 2, and the peak areas and repeatability for each component are shown in Table 1.
Favorable repeatability was obtained, with a relative standard deviation (RSD%) of 2 % max.

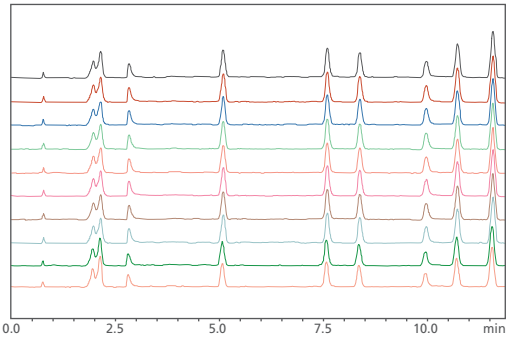


Fig. 2: Chromatograms from 10 Sequential Analyses

Table 1: Area Value (μV × sec) Repeatability

	H_2	CO	CH_4	CO_2	N_2O	C_2H_2	C_2H_4	C_2H_6
1	2263	10988	24335	26144	22263	14507	32211	45399
2	2240	10936	23998	26184	22043	14466	32808	44402
3	2280	10932	24752	26537	22435	14781	32986	44883
4	2336	10462	24032	26413	22250	14705	32386	45049
5	2237	11009	23660	26413	22515	15210	32312	45202
6	2216	11058	24172	26348	22398	14915	32909	44878
7	2230	10949	23955	27004	22604	14941	32838	45059
8	2291	10956	24687	26642	22659	14992	32871	45295
9	2253	11011	24379	26550	22426	15246	33058	45515
10	2237	11189	24741	26679	22685	15075	32792	45751
Ave.	2258	10949	24271	26491	22428	14884	32717	45143
RSD%	1.57	1.71	1.54	0.95	0.90	1.80	0.92	0.84

High-Sensitivity Analysis of Impurities in Gas

Gases used in a variety of fields, such as industrial, medical, and food, typically have to meet the established quality standards, which vary according to the application. This requires performing gas purity tests. The Shimadzu Tracera high-sensitivity gas chromatograph is equipped with a barrier discharge ionization detector (BID) that permits the simultaneous high-sensitivity analysis of inorganic gases and lower hydrocarbons. The impurity analysis of ethylene and carbon dioxide food additives using Tracera is reported here.

1. Experiments

1.1 Apparatus

Software	GCsolution
Gas chromatograph	Tracera (GC-2010 Plus A + BID-2010 Plus)
Gas sampler	MGS-2010

1.2 Conditions of Analysis

Column	Micropacked ST
Column temperature	35 °C (2.5 min) – 20 °C/min - 250 °C(0 min) - 15 °C/min - 270 °C (5.42 min) Total: 20 min
Carrier gas	He
Carrier gas control	Pressure
Pressure program	250 kPa (2.5 min) – 15 kPa/min – 400 kPa (7.5 min) (He)
Injection mode	Split (5:1)
Injection port temperature	150 °C
Detector temperature	280 °C
Discharge gas flow	He: 70 mL/min
Injection volume	1.0 mL

2. Results

2.1 Analysis of Impurities in Ethylene

Ethylene is an important chemical used as feedstock in a variety of applications and its purity is essential.

Fig. 1 shows an ethylene chromatograph. H_2 (30 ppm), CO (2 ppm), CO_2 (15 ppm), and CH_4 (30 ppm) were detected as trace impurities.

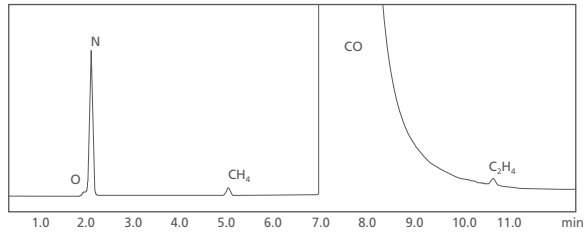


Fig. 1: Chromatograph of Impurities in Ethylene

2.2 Impurity Analysis of Carbon Dioxide Food Additive

Quality standards have been established for carbon dioxide gas used as food additives to ensure that it contains no components harmful to human health.

Fig. 2 shows the chromatogram of a carbon dioxide food additive. Trace impurities of CH_4 (2.2 ppm) and C_2H_4 (1.5 ppm) were detected.

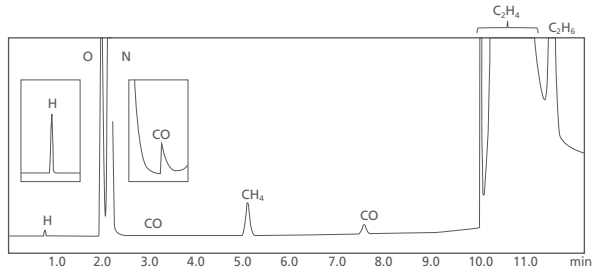


Fig. 2: Chromatograph of Impurities in Carbon Dioxide Food Additive

Trace Analysis of Carbon Dioxide in High-Purity Hydrofluorocarbon

Fluorocarbon, a generic term for organic compounds with C-F bonding, is a chemical material used as a refrigerant in refrigerators and freezers, and in air conditioners in cars, buses, other vehicles, and buildings. It is also used as a cleaning agent for electronic components and precision parts. Hydrofluorocarbon (HFC) is classified as a non-ozone-depleting chlorofluorocarbons (CFC) substitute and is used as a gas for semiconductor etching and electronic component cleaning. High-purity HFC is utilized in the semiconductor and electronics industries; confirming its purity requires measuring the concentration of impurities. In this section an example of analyzing trace quantities of CO_2 impurities in high-purity HFC using the Shimadzu "Tracera" High-Sensitivity Gas Chromatograph System is reported.

1. Experiments

1.1 Apparatus

Software	LabSolutions
Gas chromatograph	Tracera (GC-2010 Plus A + BID-2010 Plus)
Gas sampler	MGS-2010

1.2 Conditions of Analysis

Column	PoraPLOT Q (0.32 mm I.D. × 25 m, df = 10 µm)
Column temperature	*30 °C (5 min) - 40 °C/min - 100 °C (8.25 min), 15 min in total
Carrier gas	He
Carrier gas control	Constant linear velocity mode, 40 cm/sec
Injection mode	Split (10:1)
Injection port temperature	150 °C
Detector temperature	200 °C
Discharge gas	He: 50 mL/min
Injection volume	1 mL (gas sampler used)

* The initial column temperature (30 °C) can be set at a room temperature of 25 °C or lower.
Note: It is not possible to separate air components (N_2, O_2 , Ar) or CO under these analysis conditions.

2. Results

Multiple high-purity HFCs were analyzed. Fig.1 shows the resulting chromatograms, and Table 1 shows the quantitative results for CO_2. The CO_2 concentration in sample #3 was a very low, which was only 0.3 ppm. The S/N ratio was approximately 43. Conventional analysis of trace levels of CO_2 requires using an FID and a methanizer. This example demonstrates how a simply configured Tracera system can analyze trace amounts of CO_2 with high sensitivity.

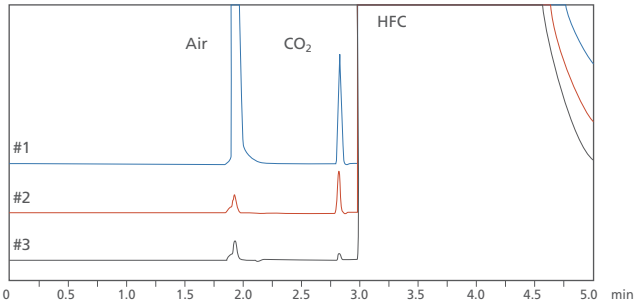


Fig. 1: Chromatograms for High-Purity HFCs

Table 1 CO_2 Quantitative Results

Sample	Quantitative Conc. (ppm)	S/N
#1	5.09	1043.5
#2	1.93	250.7
#3	0.31	43.14

Simultaneous Analysis of Evolved Gas Produced by the Degradation of a Lithium-Ion Battery

In evaluating the degradation of lithium-ion rechargeable batteries, it is necessary to analyze the gases produced inside the battery. The composition of the sampled internal gases can be investigated by conveying them to a gas chromatograph. The Shimadzu Tracera High-Sensitivity Gas Chromatograph uses a revolutionary plasma technology to detect all compounds except He and Ne. The system is capable of the simultaneous analysis of C1 to C3 hydrocarbons and inorganic gases including hydrogen, so it eliminates the conventional need for carrier gas switching or combined use of multiple systems. In addition, the Tracera's high sensitivity makes it possible to analyze small quantity gas samples. In this section, the simultaneous analysis of internal gases from a lithium-ion rechargeable battery utilizing the Tracera system is reported.

1. Experiments

1.1 Apparatus

Software	LabSolutions
Gas chromatograph	Tracera (GC-2010 Plus A + BID-2010 Plus)

1.2 Conditions of Analysis

Column	Micropacked ST
Column temperature	35 °C (2.5 min) – 20 °C /min – 250 °C (0 min) – 15 °C /min – 270 °C (5.42 min) Total.20 min
Carrier gas controller	Pressure
Pressure program	250kPa (2.5min) – 15kPa/min – 400kPa (7.5min) (He)
Injection mode	Split (1:10)
Injection port temperature	150 °C
Detector temperature	280 °C
Discharge gas flow	70 mL/min
Injection volume	50 µL

2. Results

Fig. 1 shows the chromatogram for the internal gases from a lithium-ion rechargeable battery. It is evident that the system is capable of the simultaneous analysis of C1 to C3 hydrocarbons and inorganic gases including hydrogen. The concentration ratios (%) for each component excluding oxygen and nitrogen are shown.

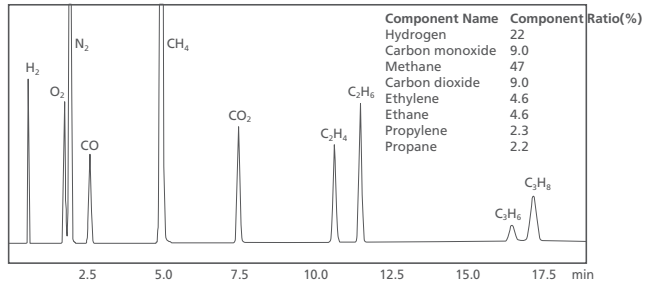


Fig. 1 Chromatogram for the internal gases from a lithium-ion rechargeable battery

Linearity for each component of the standard gas was confirmed. The concentration values for each component are shown in Table 1, and the chromatograms and calibration curves for each component are shown in Fig. 2.

Table 1 Concentrations for each component

Component name	Concentration (%)			
Hydrogen	0.962	1.92	2.89	4.81
Carbon monoxide	0.404	0.808	1.21	2.02
Methane	2.08	4.16	6.24	10.4
Carbon dioxide	0.412	0.824	1.24	2.06
Ethylene	0.204	0.408	0.612	1.02
Ethane	0.204	0.408	0.612	1.02
Propylene	0.102	0.205	0.307	0.512
Propane	0.101	0.202	0.303	0.505

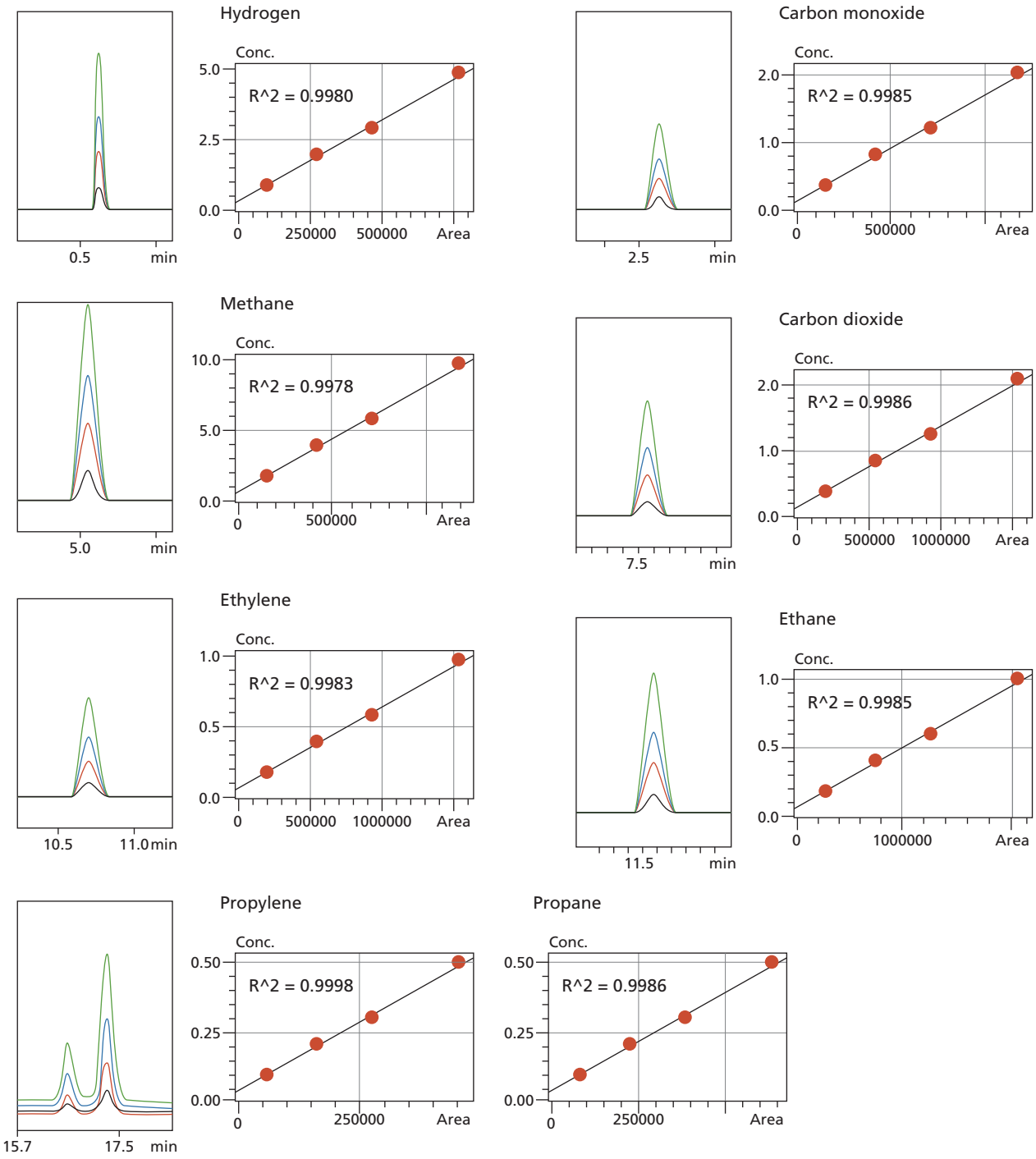


Fig. 2 Linearity for each component

Analysis of Permanent Gases Using Customized GC

A method for the analysis of permanent gases using Tracera is reported here. The analysis was done within 6 minutes.
A 2-valve-4-column system was used for the analysis. Permanent gases were analyzed with Rt-Q PLOT and Rt-MS-5A capillary columns and the BID-2010 Plus detector. The system achieved good peak area repeatability with a RSD less than 1 %. With LODs lower than 10 ppm for all analytes, the proposed method is suitable for the fast analysis of permanent gases.

Permanent gases, e.g. H_2, O_2, N_2, CO, CH_4 and CO_2, are routine analysis items in the field of gas analysis, such as the analysis of blast furnace gas, water gas, chemical industry gas, synthesis gas, and landfill gas. It is noticeably significant to gather information on these analytes and monitor their concentration variation in practical production. Currently, analytical methods in common use for the analysis of these gases often involve the hardware combination of a 2-valve-4-column switching system and two thermal conductivity detectors (TCDs) or the hardware combination of 1-valve-2-column switching system and a single thermal conductivity detector (TCD). Both have their own shortcoming(s): the former combination is of low LOD, while the latter suffers from long analysis time, narrow linear range, and low LOD.
A method is introduced in this section for fast analysis of permanent gases with the Tracera permanent gas analyzer, a 2-valve-4-column switching system, and the BID-2010 Plus detector. The method offers fast analysis speed and is capable of completing analysis of permanent gases within 6 minutes. Moreover, it offers high sensitivity, a broad linear range and good repeatability due to its barrier discharge ionization detector (BID) and the third generation AFC/APC.

1. Experiments

1.1 Apparatus

Software	GCsolution
Gas chromatograph	Tracera (GC-2010 Plus A + BID-2010 Plus)

1.2 Conditions of Analysis

Column 1	Porapak-N 1 m, 80/100 mesh
Column 2	Porapak-N 1 m, 80/100 mesh
Column 3	Rtx-MS-5A, 30 m × 0.53 mm × 50 µm
Column 4	Rt-Q PLOT, 30 m × 0.53 mm × 20 µm
Column temperature program	60 °C (8 min)
Carrier gas	He
Injection port temperature	100 °C
Injection mode	Split (3:1)
Carrier gas	High purity helium gas
Carrier gas control mode	Constant pressure, 10 mL/min
BID temperature	200 °C

2. Results and Discussion

2.1 Flow Circuit Diagram

A single channel, 2-valve, on-line automatic injecting system (as shown in the flow chart in Fig. 1) was used in the experiment: the first 10-way valve was used for the analysis of H_2, O_2, N_2, CH_4 and CO and the backflush of CO_2 and H_2O to vent; the second 10-way valve was used for the analysis of CO_2 and H_2O and the backflush of C_2+ to vent. The analytes' retention time data were as shown in Table 1.

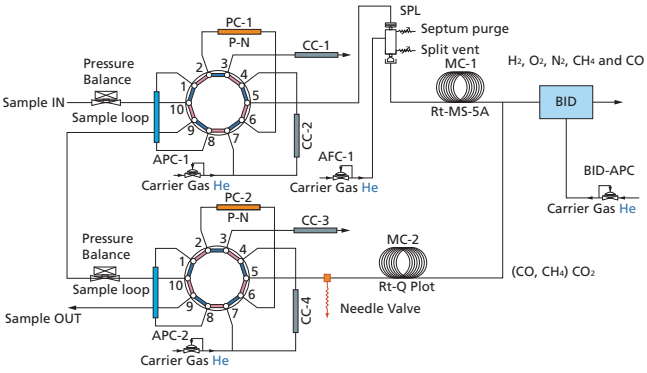


Fig. 1 Flow Circuit Diagram of the Analysis of Permanent Gases with Tracera

2.2 Chromatogram

A mixture of permanent gases standards from the Jiangsu Institute of Metrology (JSIM) was subjected to analysis under the above-mentioned conditions, yielding a chromatogram as shown below. As can be seen in Fig. 2, the analysis of the mixture of permanent gases was done within 6 minutes with satisfactory degree of separation.

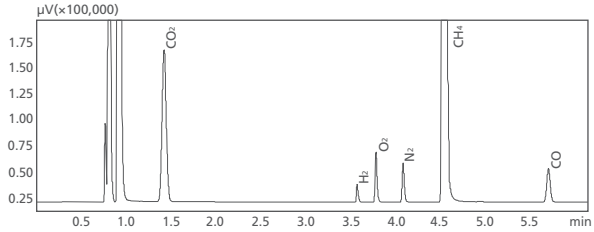


Fig. 2 Chromatogram of a Mixture of Permanent Gases (BID)

Table 1 Name, CAS No., and Retention Time of Analytes

No.	Analyte Name	CAS No.	Retention Time (min)
1	CO_2	124 - 38 - 9	1.431
2	H_2	1333 - 74 - 0	3.583
3	O_2	7782 - 44 - 7	3.792
4	N_2	7727 - 37 - 9	4.095
5	CH_4	74 - 82 - 8	4.549
6	CO	630 - 08 - 0	5.715

2.3 LOD and Repeatability

Standard permanent gases were analyzed under the above-mentioned conditions with a split ratio of 3:1. LODs were calculated as 3 times the SNR. Inorganic gases were detected with BID and their calculated LODs were as shown in Table 2. Repeatability test was performed on 6 repeated injections and the RSD% of the analytes' peak area were lower than 1 %, suggesting good area repeatability.

Table 2 Peak Area Repeatability and LODs of Analytes in Natural Gas (BID) (n=6)

No.	Analyte Name	1	2	3	4	5	6	Mean	RSD%	LOD (ppm)
1	CO_2	470032	471370	472933	472237	482767	472368	473618	0.97	1.6
2	H_2	25002	25066	24961	25096	24960	24872	24993	0.32	9.1
3	O_2	71608	71708	71596	71803	71867	71695	71713	0.15	3.3
4	N_2	59189	59303	59176	59207	59293	59074	59207	0.14	4.2
5	CH_4	6340428	6334126	6318911	6320137	6323685	6312882	6325028	0.16	4.8
6	CO	88734	88994	88791	88932	88935	88732	88853	0.13	4.8

3. Conclusion

Permanent gases were analyzed with the proposed method using Tracera. The analysis was done within 6 minutes. The experimental results showed the method had the merits of fast analysis speed, low LOD, and good repeatability. It can be satisfactorily used for the detection and analysis of permanent gases in blast furnace gas, water gas, chemical gases, synthesis gas, and landfill gas. Furthermore, Shimadzu can provide analytical apparatuses of various configurations for the analysis of permanent gases according to users' needs.

Ultrafast Analysis of Natural Gas Using Customized GC

A method for the analysis of natural gas using Tracera is reported here. The analysis was done within 5 minutes.

A 3-valve-6-column system was used for the analysis. Permanent gases were analyzed with Rt-Q PLOT and Rt-MS-5A capillary columns and the BID-2010 Plus detector, and organic hydrocarbons were analyzed with Rtx-1 and a flame ionization detector (FID). The system achieved good peak area repeatability with a RSD less than 1 %. With LODs lower than 10 ppm for hydrogen sulfide and other analytes, the proposed method is suitable for the fast analysis of natural gas. The system incorporates a Shimadzu thermal value software application.

Mainly occurring in oil fields, gas fields, coal seams and biogenetic gases, natural gas has such merits as being safe, being clean, and having a high thermal value. It mainly consists of CH_4, a few C_2-C_6 hydrocarbons, and inorganic gases such as H_2, O_2, N_2, CO, CO_2 and H_2S. Currently, the analytical method in common use for the analysis of natural gas makes use of a hardware combination of a 3-valve-4-column column switching system, packed columns, and two detectors (TCD + FID). But the system suffers from the shortcomings of long analysis time and low sensitivity.

A method is introduced in this section for the fast analysis of natural gas with a Tracera-UFNGA system, 3-valve-6-column column switching technique, and two-channel detectors (BID-2010 Plus + FID). The method offers fast analysis speed and is capable of completing analysis of permanent gases and hydrocarbons within 6 minutes. Moreover, it has high sensitivity and good repeatability due to its barrier discharge ionization detector (BID) and the third generation AFC/APC.

1. Experiments

1.1 Apparatus

Software	GCsolution
Gas chromatograph	Tracera (GC-2010 Plus A + BID-2010 Plus) +FID-2010 Plus

1.2 Conditions of Analysis

Column 1	Porapak-N 1 m, 80/100 mesh
Column 2	Porapak-N 1 m, 80/100 mesh
Column 3	OV-1 1 m, 80/100 mesh
Column 4	Rtx-MS-5A, 30 m × 0.53 mm × 50 µm
Column 5	Rt-Q PLOT, 30 m × 0.53 mm × 20 µm
Column 6	Rtx-1, 30 m × 0.32 mm × 5 µm
Column temperature program	65 °C (1 min) -10 °C/min -150 °C (3 min)
Carrier gas	He
Injection port temperature	100 °C
Injection mode	Split (3:1)
Carrier gas	High purity helium gas
Carrier gas control mode	Constant pressure, 10 mL/min
BID temperature	200 °C
FID temperature	200 °C

2. Results and Discussion

2.1 Flow Circuit Diagram

A 2-channel, 3-valve, on-line automatic injecting system (as shown in the flow chart in Fig. 1) was used in the experiment: the first 10-way valve was used for the analysis of CO_2, C_2H_4, C_2H_6, C_2H_2 and the backflush of H_2S, H_2O and C_{3+} to vent; the second 10-way valve was used for the analysis of H_2,O_2, N_2, CH_4 and the backflush of CO, CO_2 and H_2O to vent; the third 10-way valve was used for the analysis of permanent gases C_1-C_5 and C_{6+}. The retention time data were as shown in Table 1 and Table 2.

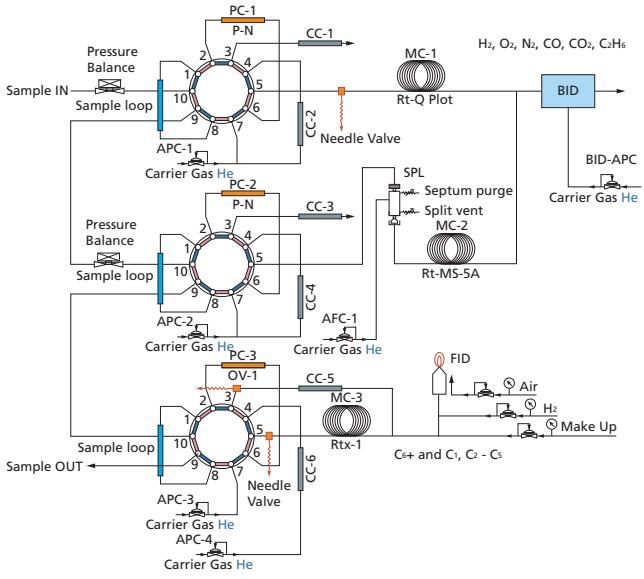


Fig. 1 Tracera-UFNGA Flow Circuit Diagram

2.2 Chromatogram

Natural gas from the Jiangsu Institute of Metrology (JSIM) was analyzed under the above-mentioned conditions, yielding a chromatogram as shown below. As can be seen in Fig. 2, the analysis of permanent gases was done within 4 minutes (or 5 minutes for H_2S-containing permanent gases) with satisfactory degree of separation. As can be seen in Fig. 3, the analysis of hydrocarbons was done with 5 minutes with satisfactory separation.

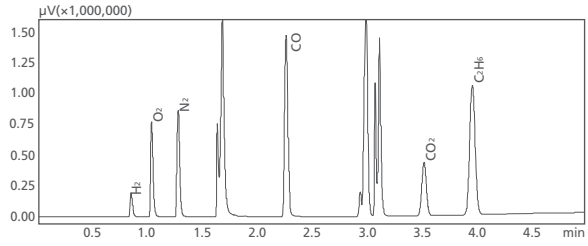


Fig. 2 Chromatogram of Natural Gas (BID)

Table 1 Name, CAS No., and Retention Time of Analytes

No.	Analyte Name	CAS No.	Retention Time (min)
1	H_2	1333 – 74 - 0	0.851
2	O_2	7782 – 44 - 7	1.037
3	N_2	7727 - 37 - 9	1.278
4	CO	630 - 08 – 0	2.257
5	CO_2	124 - 38 – 9	3.51
6	C_2H_6	74 - 84 – 0	3.95

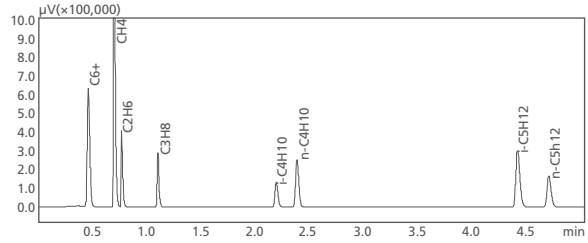


Fig. 3 Chromatogram of Natural Gas (FID)

Table 2 Name, CAS No., and Retention Time of Analytes

No.	Analyte Name	CAS No.	Retention Time (min)
1	C_{6+}	–	0.461
2	CH_4	74 - 82 - 8	0.698
3	C_2H_6	74 - 84 - 0	0.77
4	C_3H_8	74 - 98 - 6	1.105
5	i-C_4H_{10}	75 - 28 - 5	2.201
6	n-C_4H_{10}	106 - 97 - 8	2.393
7	i-C_5H_{12}	78 - 78 - 4	4.434
8	n-C_5H_{12}	109 - 66 - 0	4.723

2.3 LOD and Repeatability

Standard natural gas was subjected to analysis under the above-mentioned conditions with a split ratio of 3:1. LODs were calculated as 3 times the SNR. Inorganic gases were detected with BID and their calculated LODs were as shown in Table 3; organic gases were detected with FID with a split ratio of 22:1, yielding LODs as shown in Table 4. A repeatability test was performed on 6 repeated injections and the RSD% of the analytes' peak areas were lower than 0.5 %, suggesting good area repeatability.

Table 3 Peak Area Repeatability and LODs of Analytes in Natural Gas (BID) (n=6)

No.	Analyte Name	1	2	3	4	5	6	Mean	RSD%	LOD ppm
1	H_2	285746	285950	286403	286248	286560	284965	285979	0.20	3.08
2	O_2	1170078	1172694	1172952	1173652	1175695	1169131	1172367	0.21	1.69
3	N_2	1466695	1467881	1467961	1467563	1471331	1463375	1467468	0.17	2.83
4	CO	3122025	3130379	3134578	3131618	3134642	3122220	3129244	0.18	1.71
5	CO_2	1255938	1258067	1257917	1256841	1259091	1249675	1256255	0.27	1.13
6	C_2H_6	3674459	3679973	3679779	3676419	3681925	3654582	3674523	0.28	0.45

Table 4 Peak Area Repeatability and LODs of Analytes in Natural Gas (FID) (n=6)

No.	Analyte Name	1	2	3	4	5	6	Mean	RSD%	LOD ppm
1	C_{6+}	1057822	1055790	1057246	1059023	1058202	1057009	1057515	0.10	0.54
2	CH_4	2440959	2438491	2438997	2439966	2434848	2432038	2437550	0.14	17.72
3	C_2H_6	422883	422678	421533	422248	422136	420509	421998	0.21	2.75
4	C_3H_8	353953	353141	352740	353138	352463	352131	352928	0.18	1.94
5	i-C_4H_{10}	258055	256856	257431	257531	257013	257050	257323	0.17	2.41
6	n-C_4H_{10}	522169	519853	521389	521181	521088	520314	520999	0.16	2.17
7	i-C_5H_{12}	805206	805265	804597	805866	806000	804915	805308	0.07	1.09
8	n-C_5H_{12}	429659	429479	428971	429910	430926	429551	429749	0.15	3.57

3. Conclusion

The Shimadzu Tracera-UFNGA gas chromatograph has the merits of high sensitivity, fast analysis speed, and good repeatability and can be effectively used for the fast qualitative and/or quantitative analysis of natural gas. The Shimadzu thermal value calculation software that is incorporated in the system can automatically calculate such parameters as the thermal value, molecular weight, relative density, and Wobbe index of natural gas. Furthermore, Shimadzu can provide analytical apparatuses of various configurations for the analysis of natural gas according to users' needs.

Ultra-fast Analysis of Refinery Gas Using Customized GC

A method for the analysis of refinery gas using Tracera is reported here. The analysis was done within 6 minutes.

A 3-valve-6-column system was used for the analysis. Permanent gases were analyzed with Rt-Q PLOT and Rt-MS-5A capillary columns and the BID-2010 Plus detector, and organic hydrocarbons were analyzed with Rt-Al2O3 and a flame ionization detector (FID). The system achieved good peak area repeatability with a RSD less than 1 %. With LODs lower than 10 ppm for hydrogen sulfide and other analytes, the proposed method is suitable for the fast analysis of refinery gas. The system incorporates a Shimadzu thermal value software application.

Refinery gas is a by-product of petroleum processing. It contains a large number of utilizable lower hydrocarbons and permanent gases and can serve as a raw material for the production of various chemical products. Currently, analytical methods in common use for the analysis of refinery gas often involve the hardware combination of a 4-valve-5-column column switching system, fully packed columns, and two thermal conductivity detectors (TCDs) or the hardware combination of a 3-valve-4-column column switching system and a thermal conductivity detector (TCD) plus a flame ionization detector (FID). Analysis with the former hardware combination is more time-consuming and has lower sensitivity. The latter hardware combination uses helium as carrier gas and suffers from a narrow linear range when detecting hydrogen. Both combinations use TCD for the detection of hydrogen sulfide and the LOD of TCD is never lower than 0.1 %.

A method was introduced for the fast analysis of refinery gas with a Tracera-UFRGA system, 3-valve-6-column column switching technique, and 2-channel detectors (BID-2010 Plus + FID). The method offers fast analysis speed and is capable of completing analysis of permanent gases and hydrocarbons within 6 minutes. Moreover, it offers high sensitivity and good repeatability due to its barrier discharge ionization detector (BID) and third generation AFC/APC.

1. Experiments

1.1 Apparatus

Software	GCsolution
Gas chromatograph	Tracera (GC-2010 Plus A + BID-2010 Plus) +FID-2010 Plus

1.2 Conditions of Analysis

Column 1	Porapak-N 1 m, 80/100 mesh
Column 2	Porapak-N 1 m, 80/100 mesh
Column 3	OV-1 1 m, 80/100 mesh
Column 4	Rtx-MS-5A, 30 m × 0.53 mm × 50 µm
Column 5	Rt-Q PLOT, 30 m × 0.53 mm × 20 µm
Column 6	Rt-Al2O3 PLOT, 30 m × 0.53 mm × 10 µm
Column temperature program	65 °C (1 min) - 10 °C/min - 150 °C (3 min)
Carrier gas	He
Injection port temperature	100 °C
Injection mode	Split (3:1)
Carrier gas	High purity helium gas
Carrier gas control mode	Constant pressure, 10 mL/min
BID temperature	200 °C
FID temperature	200 °C

2. Results and Discussion

2.1 Flow Circuit Diagram

A 2-channel, 3-valve, on-line automatic injecting system (as shown in the flow chart in Fig. 1) was used in the experiment: the first 10-way valve was used for the analysis of CO_2, C_2H_4, C_2H_6, C_2H_2 and the backflush of H_2S, H_2O and C_{3+} to vent; the second 10-way valve was used for the analysis of H_2,O_2, N_2, CH_4 and the backflush of CO, CO_2 and H_2O to vent; the third 10-way valve was used for the analysis of permanent gases C_1-C_5 and C_{6+}. The retention time data were as shown in Table 1 and Table 2.

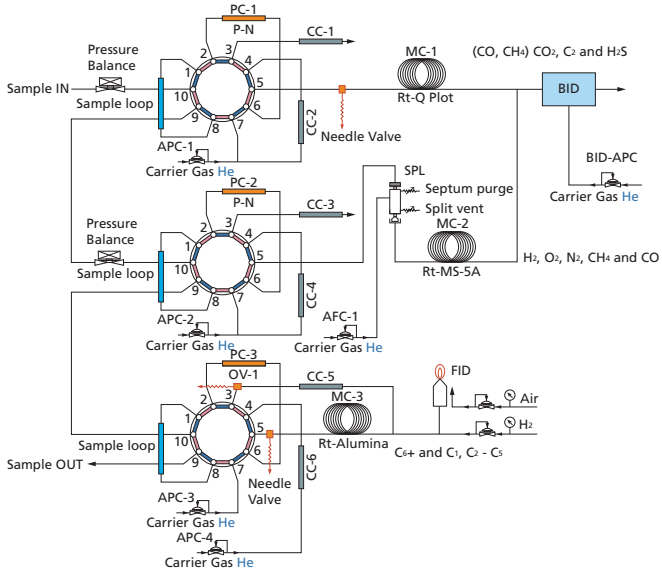


Fig. 1 Tracera-UFRGA Flow Circuit Diagram

2.2 Chromatogram

Refinery gas from the Jiangsu Institute of Metrology (JSIM) was analyzed under the above-mentioned conditions, yielding a chromatogram as shown below. As can be seen in Fig. 2, the analysis of H_2S-containing permanent gases was done within 5 minutes with satisfactory degree of separation. As can be seen in Fig. 3, the analysis of hydrocarbons was done within 5.6 minutes with satisfactory separation.

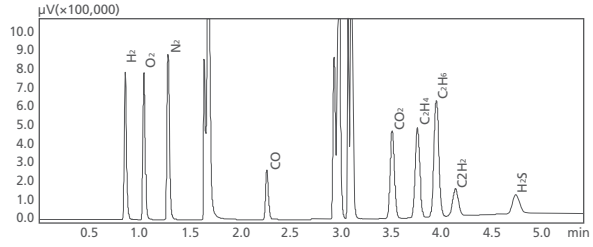


Fig. 2 Chromatogram of Refinery Gas (BID)

Table 1 Analyte Name, CAS No., and Retention Time

No.	Analyte Name	CAS No.	Retention Time (min)
1	H_2	1333 - 74 - 0	0.851
2	O_2	7782 - 44 - 7	1.038
3	N_2	7727 - 37 - 9	1.279
4	CO	630 - 08 - 0	2.263
5	CO_2	124 - 38 - 9	3.511
6	C_2H_4	74 - 85 - 1	3.762
7	C_2H_6	74 - 84 - 0	3.951
8	C_2H_2	74 - 86 - 2	4.142
9	H_2S	7783 - 6 - 4	4.743

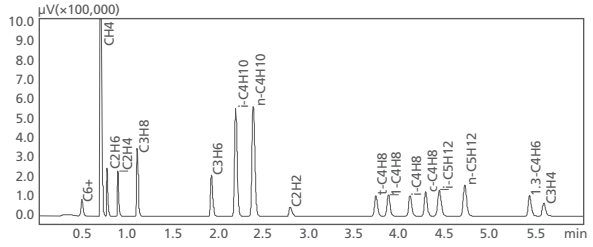


Fig. 3 Chromatogram of Refinery Gas (FID)

Table 2 Name, CAS No., and Retention Time of Hydrocarbons

No.	Analyte Name	CAS No.	Retention Time (min)
1	C_6+	-	0.509
2	CH_4	74 - 82 - 8	0.715
3	C_2H_6	74 - 84 - 0	0.785
4	C_2H_4	74 - 85 - 1	0.904
5	C_3H_8	74 - 98 - 6	1.119
6	C_3H_6	115 - 07 - 1	1.936
7	i-C_4H_{10}	75 - 28 - 5	2.201
8	n-C_4H_{10}	106 - 97 - 8	2.394
9	C_2H_2	74 - 86 - 2	2.801
10	t-C_4H_8	624 - 64 - 6	3.744
11	1-C_4H_8	106 - 98 - 9	3.881
12	i-C_4H_8	115 - 11 - 7	4.119
13	c-C_4H_8	590 - 18 - 1	4.29
14	i-C_5H_{12}	78 - 78 - 4	4.442
15	n-C_5H_{12}	109 - 66 - 0	4.723
16	1,3-C_4H_6	106 - 99 - 0	5.434
17	C_3H_4	74 - 99 - 7	5.587

2.3 LOD and Repeatability

Standard refinery gas was subjected to analysis under the above-mentioned conditions with a split ratio of 3:1. LODs were calculated as 3 times the SNR. Inorganic gases were detected with BID and their calculated LODs were as shown in Table 3; organic gases were detected with FID with a split ratio of 22:1, yielding LODs as shown in Table 4. A repeatability test was performed on 6 repeated injections and the RSD% of the analytes' peak areas were lower than 0.5 %, suggesting good area repeatability.

Table 3 Peak Area Repeatability and LODs of Analytes in Refinery Gas (BID) (n=6)

No.	Analyte Name	1	2	3	4	5	6	Mean	RSD%	LOD ppm
1	H_2	1221080	1217638	1220585	1221434	1219877	1221352	1220328	0.12	6.12
2	O_2	1201943	1201078	1203779	1201378	1199380	1203229	1201798	0.13	1.85
3	N_2	1514715	1511981	1517955	1514142	1514211	1518090	1515182	0.16	3.39
4	CO	486535	487959	489768	487103	487895	488835	488016	0.24	1.15
5	CO_2	1334791	1337904	1338552	1336785	1331065	1326637	1334289	0.35	1.24
6	C_2H_4	1510314	1513120	1514393	1512294	1504769	1499412	1509050	0.38	0.61
7	C_2H_6	2109195	2114540	2115465	2112086	2102367	2095589	2108207	0.37	0.47
8	C_2H_2	576087	576805	576730	576121	573434	571868	575174	0.35	1.03
9	H_2S	512847	508727	510989	511634	508666	511887	510792	0.34	1.51

Table 4 Peak Area Repeatability and
LODs of Analytes in Refinery Gas (FID) (n=6)

No.	Analyte Name	1	2	3	4	5	6	Mean	RSD%	LOD (ppm)
1	C_6+	158635	159528	157812	158950	157935	159468	158721	0.46	0.78
2	CH_4	2260978	2263842	2260462	2257665	2259217	2260266	2260405	0.09	15.24
3	C_2H_6	250953	252296	250088	250690	250620	251215	250977	0.30	2.62
4	C_2H_4	246691	248406	245741	246742	246307	247263	246858	0.37	2.63
5	C_3H_8	422193	423686	420984	420729	421473	422789	421976	0.27	1.87
6	C_3H_6	359603	360636	358828	358030	359391	359498	359331	0.24	2.85
7	i-C_4H_{10}	1122725	1124390	1121285	1116596	1120435	1122212	1121274	0.24	2.15
8	n-C_4H_{10}	1215908	1215589	1213446	1207766	1213136	1214267	1213352	0.24	2.14
9	C_2H_2	100365	100322	99905	99464	99998	99892	99991	0.33	6.66
10	t-C_4H_8	230623	230484	229812	228829	229949	230079	229963	0.28	2.69
11	1-C_4H_8	245654	245826	245177	244002	245320	245292	245212	0.26	2.78
12	i-C_4H_8	235678	235537	234706	233834	235066	235184	235001	0.28	2.93
13	c-C_4H_8	275596	274932	274172	273547	274261	274654	274527	0.26	2.51
14	i-C_5H_{12}	360506	360475	359229	358347	358743	358699	359333	0.26	2.24
15	n-C_5H_{12}	409180	408223	408125	406197	407397	407559	407780	0.24	1.93
16	1,3-C_4H_6	245078	244855	244317	243179	244158	244869	244409	0.29	2.97
17	C_3H_4	166867	166934	166314	165446	166053	166660	166379	0.34	4.79

3. Conclusion

The Shimadzu Tracera-UFRGA gas chromatograph has the merits of high sensitivity, fast analysis speed, and good repeatability and can be effectively used for the fast qualitative and/or quantitative analysis of refinery gas. The Shimadzu thermal value calculation software that is incorporated in the system can automatically calculate such parameters as the thermal value, molecular weight, relative density, and Wobbe index of refinery gas. Furthermore, Shimadzu can provide analytical apparatuses of various configurations for the analysis of refinery gas and extended refinery gas according to users' needs.

Analysis of Extended Refinery Gas Using Customized GC

A method for the analysis of extended refinery gas C1-C13 using Tracera is reported here. The analysis was done within 10 minutes. A 4-valve-7-column system was used for the analysis. Permanent gases were analyzed with Rt-Q PLOT and Rt-MS-5A capillary columns and the BID-2010 Plus detector; organic hydrocarbons C_1-C_5, C_6+ were analyzed with Rt-Al2O3 and a flame ionization detector 1 (FID1) and hydrocarbons C_6-C_{13} were analyzed with Rtx-1 and a flame ionization detector 2 (FID2). The system achieved good peak area repeatability with a RSD less than 1 %. With LODs lower than 10 ppm for hydrogen sulfide and other analytes, the proposed method is suitable for fast analysis of extended refinery gas. The system incorporates a Shimadzu thermal value software application.

Refinery gas is a by-product of petroleum processing. It contains a lot of utilizable lower hydrocarbons and permanent gases and can serve as a raw material for the production of various chemical products. The composition of refinery gas and concentration ranges of its components vary significantly with the place of origin of the refinery gas. Trace heavy hydrocarbons C_6-C_{13} in refinery gas were included as items to be assayed according to GPA-2286.

A method was introduced for the fast analysis of refinery gas with the Tracera-ERGA system, 4-valve-7-column column switching technique, and 3-channel detectors (BID-2010 Plus + 2 FIDs). The method offers fast analysis speed and is capable of completing analysis of permanent gases and hydrocarbons within 10 minutes. Moreover, it offers high sensitivity and good repeatability due to its barrier discharge ionization detector (BID) and the third generation AFC/APC.

1. Experiments

1.1 Apparatus

Software	GCsolution
Gas chromatograph	Tracera (GC-2010 Plus A + BID-2010 Plus) +FID-2010 Plus × 2

1.2 Conditions of Analysis

Column 1	Porapak-N 1 m, 80/100 mesh
Column 2	Porapak-N 1 m, 80/100 mesh
Column 3	OV-1 1 m, 80/100 mesh
Column 4	Rtx-MS-5A, 30 m × 0.53 mm × 50 µm
Column 5	Rt-Q PLOT, 30 m × 0.53 mm × 20 µm
Column 6	Rt-Al_2O_3 PLOT, 30 m × 0.53 mm × 10 µm
Column 7	Rtx-1, 30 m × 0.32 mm × 5 µm
Column temperature program	65 °C (1 min) - 10 °C/min - 150 °C (6 min)
Carrier gas	He
Injection port temperature	100 °C
Injection mode	Split (3:1)
Carrier gas	High purity helium gas
Carrier gas control mode	Constant pressure, 10 mL/min
BID temperature	200 °C
FID 1 temperature	200 °C
FID 2 temperature	200 °C

2. Results and Discussion

2.1 Flow Circuit Diagram

A 2-channel, 3-valve, on-line automatic injecting system (as shown in the flow chart in Fig. 1) was used in the experiment: the first 10-way valve was used for the analysis of CO_2, C_2H_4, C_2H_6, C_2H_2 and the backflush of H_2S, H_2O and C_3+ to vent; the second 10-way valve was used for the analysis of H_2, O_2, N_2, CH_4 and the backflush of CO, CO_2 and H_2O to vent; the third 10-way valve was used for the analysis of permanent gases C_1-C_5 and C_6+; the fourth 10-way valve was used for the analysis of C_6-C_{13}. The retention time data were as shown in Table 1, Table 2, and Table 3.

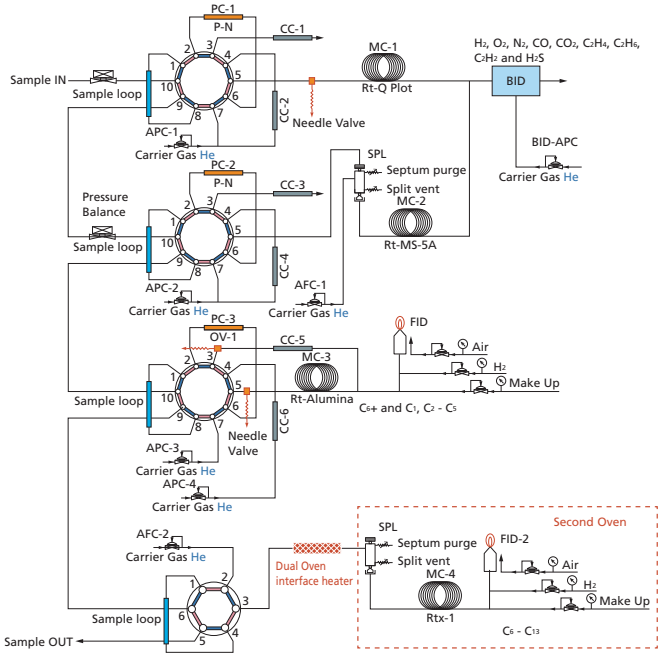


Fig. 1 Tracera-ERGA Flow Circuit Diagram

2.2 Chromatogram

Refinery gas from the Jiangsu Institute of Metrology (JSIM) was analyzed under the above-mentioned conditions, yielding a chromatogram as shown below. As can be seen in Fig. 2, the analysis of H_2S-containing permanent gases was done within 5 minutes with satisfactory degree of separation. As can be seen in Fig. 3, the analysis of hydrocarbons was done within 5.6 minutes with satisfactory separation. As can be seen in Fig. 4, the analysis of C_6-C_{13} was done within 10 minutes with satisfactory separation.

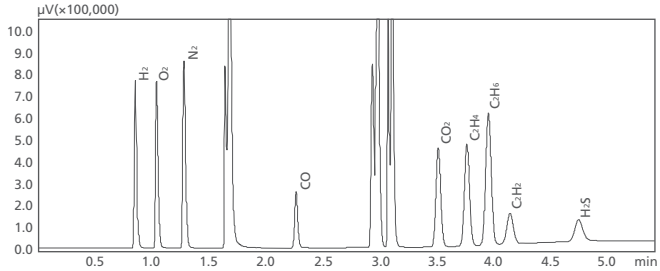


Fig. 2 Chromatogram of Refinery Gas (BID)

Table 1 Name, CAS No., and Retention Time of Analytes

No.	Analyte Name	CAS No.	Retention Time (min)
1	H_2	1333 - 74 - 0	0.851
2	O_2	7782 - 44 - 7	1.038
3	N_2	7727 - 37 - 9	1.279
4	CO	630 - 08 - 0	2.263
5	CO_2	124 - 38 - 9	3.511
6	C_2H_4	74 - 85 - 1	3.762
7	C_2H_6	74 - 84 - 0	3.951
8	C_2H_2	74 - 86 - 2	4.142
9	H_2S	7783 - 6 - 4	4.743

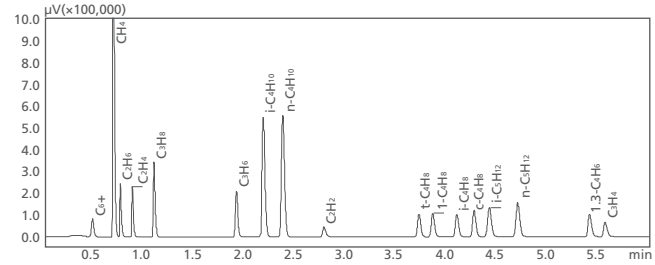


Fig. 3 Chromatogram of Refinery Gas (FID1)

Table 2 Name, CAS No., and Retention Time of Hydrocarbons C1-C6

No.	Analyte Name	CAS No.	Retention Time (min)
1	C_6+	-	0.509
2	CH_4	74 - 82 - 8	0.715
3	C_2H_6	74 - 84 - 0	0.785
4	C_2H_4	74 - 85 - 1	0.904
5	C_3H_8	74 - 98 - 6	1.119
6	C_3H_6	115 - 07 - 1	1.936
7	i-C_4H_{10}	75 - 28 - 5	2.201
8	n-C_4H_{10}	106 - 97 - 8	2.394
9	C_2H_2	74 - 86 - 2	2.801
10	t-C_4H_8	624 - 64 - 6	3.744
11	1-C_4H_8	106 - 98 - 9	3.881
12	i-C_4H_8	115 - 11 - 7	4.119
13	c-C_4H_8	590 - 18 - 1	4.29
14	i-C_5H_{12}	78 - 78 - 4	4.442
15	n-C_5H_{12}	109 - 66 - 0	4.723
16	1,3-C_4H_6	106 - 99 - 0	5.434
17	C_3H_4	74 - 99 - 7	5.587

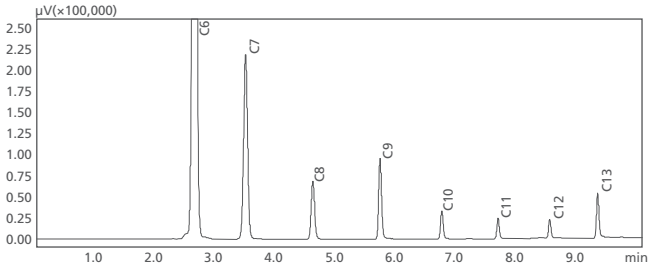


Fig. 4 Chromatogram of Refinery Gas (FID2)

Table 3 Name, CAS No., and Retention Time of Hydrocarbons C6-C13

No.	Analyte Name	CAS No.	Retention Time (min)
1	C_6H_{14}	107 - 83 - 5	2.672
2	C_7H_{16}	142 - 82 - 5	3.523
3	C_8H_{18}	111 - 65 - 9	4.639
4	C_9H_{20}	921 - 47 - 1	5.753
5	$C_{10}H_{22}$	1072 - 16 - 8	6.777
6	$C_{11}H_{24}$	17302 - 28 - 2	7.709
7	$C_{12}H_{26}$	1632 - 71 - 9	8.569
8	$C_{13}H_{28}$	17312 - 77 - 5	9.363

2.3 LOD and Repeatability

Standard refinery gas was subjected to analysis under the above-mentioned conditions with a split ratio of 3:1. LODs were calculated as 3 times the SNR. Inorganic gases were detected with BID and their calculated LODs were as shown in Table 4; some organic gases were detected with FID1 with a split ratio of 22:1, yielding LODs as shown in Table 5; some organic gases were detected with FID2 with a split ratio of 20:1, yielding LODs as shown in Table 6. A repeatability test was performed on 6 repeated injections and the RSD% of the analytes' peak areas were lower than 0.5 %, suggesting good area repeatability.

Table 4 Peak Area Repeatability and LODs of Analytes in Refinery Gas (BID) (n=6)

No.	Analyte Name	1	2	3	4	5	6	Mean	RSD%	LOD ppm
1	H_2	1221080	1217638	1220585	1221434	1219877	1221352	1220328	0.12	6.12
2	O_2	1201943	1201078	1203779	1201378	1199380	1203229	1201798	0.13	1.85
3	N_2	1514715	1511981	1517955	1514142	1514211	1518090	1515182	0.16	3.39
4	CO	486535	487959	489768	487103	487895	488835	488016	0.24	1.15
5	CO_2	1334791	1337904	1338552	1336785	1331065	1326637	1334289	0.35	1.24
6	C_2H_4	1510314	1513120	1514393	1512294	1504769	1499412	1509050	0.38	0.61
7	C_2H_6	2109195	2114540	2115465	2112086	2102367	2095589	2108207	0.37	0.47
8	C_2H_2	576087	576805	576730	576121	573434	571868	575174	0.35	1.03
9	H_2S	512847	508727	510989	511634	508666	511887	510792	0.34	1.51

Table 5 Peak Area Repeatability and LODs of Analytes in Refinery Gas (FID1) (n=6)

No.	Analyte Name	1	2	3	4	5	6	Mean	RSD%	LOD ppm
1	C_6+	158635	159528	157812	158950	157935	159468	158721	0.46	0.78
2	CH_4	2260978	2263842	2260462	2257665	2259217	2260266	2260405	0.09	15.24
3	C_2H_6	250953	252296	250088	250690	250620	251215	250977	0.30	2.62
4	C_2H_4	246691	248406	245741	246742	246307	247263	246858	0.37	2.63
5	C_3H_8	422193	423686	420984	420729	421473	422789	421976	0.27	1.87
6	C_3H_6	359603	360636	358828	358030	359391	359498	359331	0.24	2.85
7	i-C_4H_{10}	1122725	1124390	1121285	1116596	1120435	1122212	1121274	0.24	2.15
8	n-C_4H_{10}	1215908	1215589	1213446	1207766	1213136	1214267	1213352	0.24	2.14
9	C_2H_2	100365	100322	99905	99464	99998	99892	99991	0.33	6.66
10	t-C_4H_8	230623	230484	229812	228829	229949	230079	229963	0.28	2.69
11	1-C_4H_8	245654	245826	245177	244002	245320	245292	245212	0.26	2.78
12	i-C_4H_8	235678	235537	234706	233834	235066	235184	235001	0.28	2.93
13	c-C_4H_8	275596	274932	274172	273547	274261	274654	274527	0.26	2.51
14	i-C_5H_{12}	360506	360475	359229	358347	358743	358699	359333	0.26	2.24
15	n-C_5H_{12}	409180	408223	408125	406197	407397	407559	407780	0.24	1.93
16	1,3-C_4H_6	245078	244855	244317	243179	244158	244869	244409	0.29	2.97
17	C_3H_4	166867	166934	166314	165446	166053	166660	166379	0.34	4.79

Table 6 Peak Area Repeatability and LODs of Analytes in Refinery Gas (FID2)(n=6)

No.	Analyte Name	1	2	3	4	5	6	Mean	RSD%	LOD ppm
1	C_6H_{14}	5546550	5553548	5535946	5541872	5546550	5546550	5545169	0.11	2.78
2	C_7H_{16}	1018848	1028846	1023021	1019161	1028345	1028345	1024428	0.46	1.24
3	C_8H_{18}	271844	272315	273850	274521	273765	275368	273611	0.48	2.83
4	C_9H_{20}	330625	331098	330956	330576	331289	331963	331084	0.15	1.93
5	$C_{10}H_{22}$	102720	103219	102187	103165	102267	102980	102756	0.43	1.54
6	$C_{11}H_{24}$	71138	71563	71765	71237	71986	71683	71562	0.45	2.73
7	$C_{12}H_{26}$	62221	62976	62367	62843	62356	62667	62572	0.48	3.13
8	$C_{13}H_{28}$	163457	162980	162789	163126	163583	162891	163138	0.20	3.76

3. Conclusion

The Shimadzu Tracera-ERGA gas chromatograph has the merits of high sensitivity, fast analysis speed, and good repeatability and can be used effectively for the fast qualitative and/or quantitative analysis of refinery gas. The Shimadzu thermal value calculation software that is included in the system can automatically calculate such parameters as the thermal value, molecular weight, relative density, and Wobbe Index of refinery gas. Furthermore, Shimadzu can provide single oven analytical apparatuses for the analysis of extended refinery gas and other analytical apparatuses of various configurations for the analysis of refinery gas according to users' needs.