INSTRUCTION MANUAL
TOTAL ORGANIC CARBON ANALYZER
MODEL TOC-5000

SHIMADZU CORPORATION

ENVIRONMENTAL ANALYSIS INSTRUMENTS PLANT
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1. INTRODUCTION

Thank you for having purchased Shimadzu Total Organic Carbon
Analyzer model TOC-5000.

This analyzer measures total carbon (TC), inorganic carbon (IC)
and total organic carbon (TOC) in water. Its operation is based
on the combustion/non-dispersive infrared gas analysis method
widely employed for TOC measurement.

Prior to using the TOC-5000, please read through and fully under-
stand this instruction manual for proper operation. After reading
the manual, retain it at your hand so that you can refer to it at
any time as necessary.

1.1 Precautions on Use

Observe the following precautionary requirements in operating the
equipment:

1) Do not touch parts near the TC furnace center (around combustion
   tube inlet) when TC furnace is being heated; the parts are very
   hot. —— To avoid being burnt

2) When raising the TC furnace temperature, be sure to flow
   carrier gas in advance. This is for prevention of back-
   flow of high-sensitivity catalyst into the upper area.

3) Prior to disconnecting or replacing TC combustion tube, be sure
   to lower the TC furnace temperature sufficiently enough to avoid
   burn. If it is inevitable to manipulate the tube with the fur-
   nace kept at a high temperature, take a necessary safety measure
   such as wearing anti-heat gloves. —— To avoid being burnt

4) Be sure to mount combustion tube when heating up TC furnace.
   If it is necessary to heat it up without the tube, dismount TC
   injection port fitting (white plastic part) or plug the furnace
   center hole with quartz wool or the like adiabatic material to
   prevent the part from being deformed by radiation heat of the
   TC furnace center (about 680°C). —— To prevent damage on parts

5) To make drainage resistance as small as possible, place the end
   of an external drain tubing connected to the drain port of the
   equipment right panel in the atmosphere near the equipment,

and ensure that the tubing is placed at a lower level than the drain port. Large resistance could hamper satisfactory drainage, causing drainage to overflow inside the equipment. —— To prevent corrosion of parts
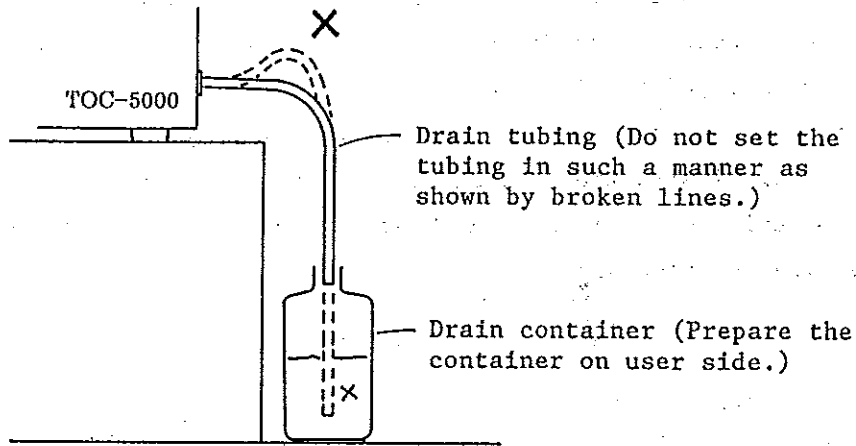
Fig. 1.1 Connection of Drain Tubing

6) When operating the analyzer (when supplying carrier gas), be sure to set the three-way cock lever in the lower part of IC reaction vessel at the left position. If carrier gas were supplied with the lever set at the lower position, carrier gas pressure (5 to 6 kg/cm^2) would be applied to the flow line before the three-way cock, possibly causing joints to be disconnected or damaging parts (including combustion tube).
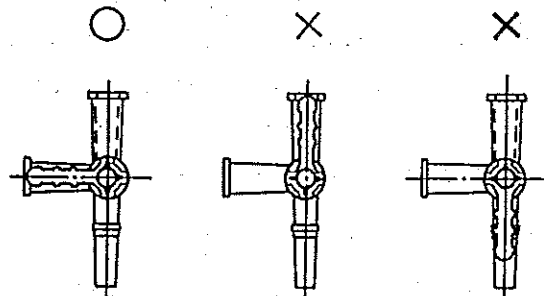
With the lever at this position, carrier gas would be discharged outside the equipment before it reaches IC reaction vessel. (Select this position only when disconnecting IC reaction vessel with solution in it.)

Absolutely do not set the lever at this position.

Fig. 1.2 Setting Position of Three-way Cock in the Lower Part of IC Reaction Vessel

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7) On 「GENERAL CONDITIONS」 screen, conduct measurement after setting the microliter syringe size and the TC catalyst type actually used in the analyzer. Inconsistent settings can cause erroneous measurement or even damage parts (including combustion tube). ── To prevent erroneous measurement and damage on parts

8) When water level rises due to insufficient drainage of the IC reaction vessel, it is suspected that the drainage-discharging silicon tube remains flat when the pinch valve is opened, thus preventing drainage from flowing. So, check the tube. (Refer to Para. 7.3.11 of the Instruction Manual.) ── To prevent erroneous measurement

9) When stopping the equipment, do not turn off the power switch directly. Designate FINISH on 「STANDBY OPTIONS」 screen and follow the instruction shown on the screen. (TC furnace is turned off first. After 30 minutes or longer period, turn off the power switch.) This rule does not apply in an emergency case. ── To prevent deterioration of durability of TC injection port fitting

10) After measuring sample which contains large amount (about 1,000 ppm or more) of acid or salt, if equipment is left with sample remaining in the sample injection needle, the needle may be corroded by sample or clogged with precipitated salt. To prevent this, execute TC and IC WASHING with sampling tube end put in water, using MECHANICAL CHECK function on 「MAINTENANCE」 screen. (See Fig. 5.4.) ── To prevent corrosion and clogging of sample injection needle

11) For mounting, tighten connectors connecting to the 4-port valve of the sample injector with fingers. If they should be tightened too strong using a tool, note carefully that excessive force is applied to the inside valve body, causing deformation, and leak may occur in the valve.

1.2 Specifications

Measuring object	TC, IC, TOC (TC-IC), NPOC*
Method	Combustion/non-dispersive infrared gas analysis method
Combustion temperature	680°C
Range	4 ppb to 4,000 ppm (4 ppb to 5,000 ppm for IC)
Analysis time	Normally 2 to 3 minutes for TC or IC (At the maximum, 4.5 minutes for TC and 3.5 minutes for IC)
Repeatability	Less than 2,000 ppm (Less than 2,500 ppm for IC): Standard deviation is within 1% of the full-scale range. 2,000 to 4,000 ppm (2,500 to 5,000 ppm for IC): Standard deviation is within 2% of the full-scale range.
Sample introduction method	Introduction with automatic injector
Sample injection volume	Variable between 50 and 2,000 µℓ (with 2,500 µℓ micro-liter syringe) Variable between 4 and 250 µℓ (with 250 µℓ microliter syringe)
Pretreatment method for IC	With automatic sparging
Carrier gas	High purity air (filled in a cylinder) Pressure : Approx. 6 kgf/cm² (Max. 7 kgf/cm²) Flow rate: 150 mℓ/min. (300 mℓ/min. including sparging gas)

CPU function
  Signal processing
 	
  Data processing
 	
  Control
 	
  Others
	Linearization, baseline correction, peak detection/area calculation
	 Concentration calculation by one to four-point calibration curve methods, automatic selection of optimum calibration curve from three calibration curves, filing of up to 18 calibration curves, automatic deletion of abnormal values and automatic additional measurement and calculation thereof, SD/CV calculation, and repeated measurement with automatic change in the range and sample injection volume
	 Sample injector movements, TC furnace temperature, and on/off of carrier gas and sparge gas
	 Automatic selection of optimum measuring condition, maintenance/check functions, abnormality detection, and timer reservation for re-start

Display	LCD (white liquid crystal with backlight) 640 × 400 dots, 88 characters × 22 lines
Printer	240 dots for graphic, 40 characters/line, Chart width 110 mm, Thermosensitive type
Ambient temperature	5 ∿ 35°C
Power requirements	AC 100, 110, 115, 120, 127, 220, 230 or 240 V as ordered, ±10%, 5 A (Ordinary power consumption: About 300 VA), 50 – 60Hz
Outside dimensions	About 480W × 520D × 480H (mm) (Excluding protrusions)
Weight	About 46 kg

* NPOC (Non-Purgeable Organic Carbon): TOC measured after sparging

2. INSTALLATION

2.1 Inspection of Parts

After unpacking, check that the package contains all of the following parts:

Table 2.1 Standard Accessories

Part Name	Part No.	Q'ty	Remarks
Accessory kit	638-90217-03 or 638-90217-05	1	-03: for UL, CSA -05: for Europe
[Breakdown]			
1. Pallet	638-14305	1	Refer to Para. 5.1.9.
2. Humidifier	638-52813	1	Refer to Para. 5.1.2.
3. CO_2 absorber	630-00999	1	Refer to Para. 5.1.3.
4. Shaft	631-28177	1	Refer to Para. 5.1.7.
5. Chart paper	630-08913	1	Refer to Para. 5.1.7.
6. Connecting cord	071-60814-01 (for UL, CSA) or 071-60814-02 (for Europe)	1	Refer to Para. 2.4.
7. Combustion tube	631-41524	2	Refer to Para. 5.1.4. through 5.1.6.
8. TC catalyst set	638-92069-01	1	Refer to Para. 5.1.4.
9. High sensitivity TC catalyst set	638-92070-01	1	Refer to Para. 5.1.5.
10. IC reagent	630-00710	1	Refer to Para. 5.1.9.
11. IC reagent container	630-02657	1	Refer to Para. 5.1.9.
12. O-ring for adapter	036-11216	1	Refer to Para. 5.1.9.
13. Microliter syringe, 250 μℓ	630-02591-04	1	Refer to Para. 5.1.8.
14. Microliter syringe, 2,500 μℓ	630-02591-07	1	Refer to Para. 5.1.8.
15. Half union, S304, 1/8 CM4	035-55026-02	1	Refer to Para. 2.7.
16. Name plate for LCD	631-51959	1	Refer to Para. 5.1.11.
17. Plastic tube, 8 mm ID, 11 mm OD	630-00315-08	2 m	Refer to Para. 2.7.
18. Sparging tube pack	630-00337	1	Refer to Para. 6.6.
19. Catalyst filling stick	638-16023	1	Refer to Para. 5.1.5.
20. Cleaning wire, for needle	638-30002	1	Refer to Para. 7.3.9.
21. O-ring, 4D P10A	036-11209	1	Refer to Para. 7.3.12.
22. O-ring, Teflon P10	036-11408	1	Refer to Para. 7.3.12.
23. O-ring, AS568A-116	630-01566	1	Refer to Para. 7.3.12.
24. O-ring, 4D P22	036-11222	1	Refer to Para. 7.3.12.
25. Needle	630-01565	2	Refer to Para. 7.3.9.
26. Plunger tip for 250 μℓ	630-02546-45	1	Refer to Para. 7.3.8.
27. Plunger tip for 2,500 μℓ	630-02546-49	1	Refer to Para. 7.3.8.
28. Flare pipe, 0.5 mm ID, 1.5 mm OD, 400 mm long	638-41269	1	Refer to Para. 7.3.9.
29. 2N-hydrochloric acid	630-00998	1	Refer to Para. 7.2.1.
30. Silicone grease (for high vacuum)	017-30812-01	1	Refer to Para. 5.1.6. Refer to Para. 5.1.10.

Part Name	Part No.	Q'ty	Remarks
32. Potassium hydrogen phthalate 25 g	630-00635-01	1	Refer to Para. 5.1.12.
33. Sodium carbonate 25 g	630-00962-01	1	Refer to Para. 5.1.12.
34. Sodium hydrogen carbonate 25 g	630-00963-01	1	Refer to Para. 5.1.12.
35. Fuse, for transformer	638-69095	1	
Instruction Manual	M393-0085	1	

Table 2.2 Optional Accessories

Part Name	Part No.	Remarks
Adsorption type gas purifier	638-52824-02	These parts may be prepared on user side. Particularly, it is recommended to prepare a high purity air cylinder on user side.
High purity air cylinder	630-00960	
Cylinder pressure regulator	630-08585-05	
Air piping set (with nylon tube, 20 m)	638-41204	
Microliter syringe, 500 μℓ	630-02591-05	Select appropriate type according to the intended injection volume.
Microliter syringe, 1,000 μℓ	630-02591-06	
Plunger tip (3 pcs. in a set)	638-60734-06	For 500 μℓ microliter syringe
Plunger tip (3 pcs. in a set)	638-60734-07	For 1,000 μℓ microliter syringe
RS-232C interface 25P	638-72376-02	For output to RS-232C
RS-232C interface 9P	638-72376-03	For output to RS-232C (For IBM PC/AT and its compatible computers)
Optional board connection set	638-70292	Required for mounting RS-232C interface.
Suspended particle kit S	638-90245-01	Tubing and injection parts for particle sizes up to 0.5mm and up to 0.8mm diameter
External printer cable set	638-70345	For the connection of an external printer

Parts listed in Table 2.2 above are optional. Place an order for
any of these parts separately if required.

The parts denoted with the numbers 1 through 19 in Table 2.1 are
delivered as disconnected, although they are to be mounted on the
equipment. See the paragraph indicated on the "Remarks" column
for mounting method of each part.

Table 2.3 below is a list of consumable parts or parts with rela-
tively low durability. It is recommended to keep these parts always
in stock for convenience in replacement.

Table 2.3 Spare Parts

Part Name	Part No.	Remarks
Combustion tube	631-41524	TC combustion tube
Platinum catalyst, 20 g	017-42801-01	Replacement catalyst for TC catalyst set
High sensitivity TC catalyst	630-00996	Replacement catalyst for high sensitivity TC catalyst set
Chart paper	630-08913-01	For printer (10 rolls in a carton)
O-ring, 4D P10A	036-11209-84	5 pcs. in a set
O-ring, Teflon P10	036-11408-84	5 pcs. in a set
O-ring, AS568A-116	630-01566	1 pc. in a set
O-ring, 4D P22	036-11222-84	5 pcs. in a set
Gasket for injection needle	631-43404-84	5 pcs. in a set
Needle	630-01565	For sample injection
Filter capillary type	630-02655	For sampling
Microliter syringe, 250 µℓ	630-02591-04	
Microliter syringe, 2,500 µℓ	630-02591-07	
Plunger tip (3 pcs. in a set)	638-60734-05	For 250 µℓ syringe
Plunger tip (3 pcs. in a set)	638-60734-08	For 2,500 µℓ syringe
Halogen scrubber	630-00992	
Sleeve set 6F-T	035-62994-03	Teflon-made, for TC combustion tube outlet joint
CO_2 absorber	630-00999	For purifying purge gas for NDIR optical system
IC reagent	630-00710	
Fuse, for transformer	638-69095	

2.2 Location for Installation

The TOC-5000 is designed for installation on a desk or the like bench and for operation through an LCD and a keyboard.

The outside dimensions are shown in Fig. 2.1. For convenience of operation and maintenance, a space of about 1 m width is required for installation.

In lifting the equipment, hold the lateral sides of the bottom panel with both hands.
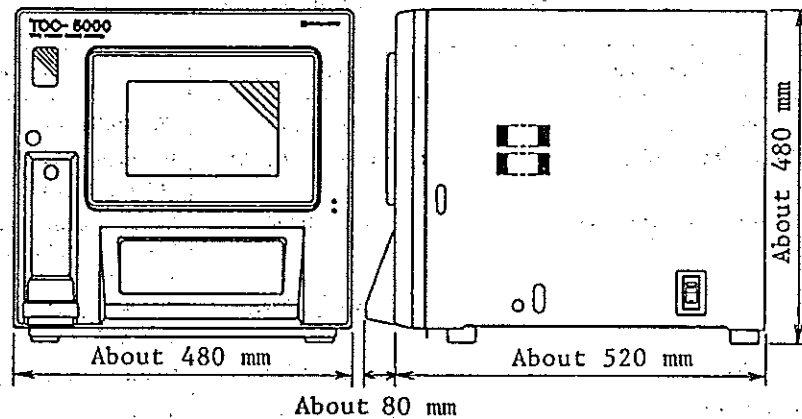
Fig. 2.1   Outside Dimensions of TOC-5000

2.3   Environmental Conditions of Installation Site

1) Select a clean area free from corrosive or organic gas and dust. For high sensitivity measurement in particular, soiled atmosphere would cause erroneous measurement.

2) Place the equipment on a vibration- and impact-free, horizontal, rigid desk.

3) Ambient temperature must be stable.   Do not install the equipment in a place exposed to direct sunlight, radiation by heat source and/or wind from air-conditioner.

4) Do not install the equipment where use of fire is prohibited.

5) Do not install in the vicinity of a source of intensive magnetic or electric field or high frequency.

6) Select a place where stable power supply is available and proper grounding is possible.

2.4   Removal of Transportation Fixtures and Screws

Equipment is packed using transportation fixtures and screws.
Be sure to unpack equipment in the following procedure.
Please note that equipment must be packed, fixed with these fixtures and screws when it is transported.

1) Remove fixing screws (2 pcs.) at the back side of top cover to open it and remove two foamed styrene packings inside the equipment.

2) Open the front door and remove foamed styrene packing in the lower part of the TC furnace.

3) Remove LCD unit fixing screws (2 pcs.) in the rear of the front door.

4) The sampling tube with the sampling needle, protruding from a hole in the front door, is covered with a Teflon tube (inside diameter: 2 mm, outside diameter: 3 mm) for protection during transportation. Remove this Teflon tube during operation. The Teflon tube can be used as sparging tube. (See Para. 5.1.14.)

2.5 Power Connection and Grounding

This equipment is preset to either of the specified source voltages before shipment. The selected voltage is indicated on the label attached on the lower panel at rear of the equipment.

Check that the source voltage to be used corresponds with that indicated on label before connection of the power cord.

Connect the equipment to a stable power supply as much as possible with sufficient capacity. With unstable voltage, high sensitivity measurement may be inversely affected.

This equipment can be operated with either of the frequencies, 50 Hz and 60 Hz.

Power cord contained in standard accessories is three-wire cable including grounding wire and equipped with 2P (grounding type) plug at the end.

Complete grounding is essential not only for safety but also for protecting the logic circuit and microcomputer from disturbing noises.

The power switch of the equipment uses a thermal breaker and not a fuse. If overcurrent flows, the switch will be turned off automatically. The equipment can be powered again simply by turning on the switch. However, if the switch is frequently turned off, it is necessary to locate the cause of overcurrent and take a necessary preventive measure.

2.6 Change of Supply Voltage

Prior to shipment, the equipment has been set to be operable with
the supply voltage available in the destination. When supply volt-
age is changed, it may be necessary to change the wiring connection
to the supply voltage-adjusting terminal board and the settings on
the main board to conform to a new supply voltage. Therefore, be
sure to contact our local agent or office when change of supply
voltage is needed.

2.7 Gas Connection

Normally the equipment uses cylinder-filled high purity air as
carrier gas (also as combustion-supporting gas).
High purity air, which is a composite air made of pure nitrogen
and pure oxygen, shall not contain more than 1 ppm of CO_2, CO and
HC (hydrocarbon), respectively.
Carrier gas containing more than 1 ppm of these impurities would
impair the measurement accuracy. The influence on the measurement
accuracy by impure carrier gas is large particularly in high sen-
sitivity measurement.
Carrier gas with more than 1 ppm of impurities can be used if it
is purified by an adsorption type gas purifier (optional accessory
P/N: 638-52824-01). However, since this gas purifier utilizes the
adsorptive property of molecular Sieves 13X (synthetic zeolite),
it can purify only limited types of gas; gas containing hard-to-
adsorb organic components (molecules of an effective diameter
larger than 10 Å) or gas with too much impurity cannot be purified
sufficiently and deteriorate the adsorption performance of the
purifier in a short period. Therefore, the impurity content of
carrier gas to be supplied to the equipment should be as small as
possible. The life of purifier is shortened particularly when
carrier gas with high moisture content is used. In view of this,
use cylinder-filled gas (cylinder gas provides a low dew point).
Absolutely do not use air direct from a compressor.
Even with high purity gas which assuredly satisfies the above re-
quirements on impurity concentration, it is recommended to use an
adsorption type gas purifier to ensure stable measurement.

Connect a pressure regulator to the gas cylinder to ensure stable gas supply of about 6 kg/cm^2 (7 kg/cm^2 at the maximum) to the gas inlet of the equipment. $\Rightarrow = 85$ psi

Connect the pressure regulator with the equipment via nylon tubing (4 mm O.D., 2.5 mm I.D.). The air piping set found in the optional accessories list (Table 2.2) contains nylon tubing and connection parts (two half unions). Attach the half unions each to the carrier gas inlet of the equipment and the pressure regulator outlet (PT1/4), and insert nylon tubing to the half unions by force. For disconnection, pull the tubing while pressing the green ring of the half union with a minus driver. Do not bend piping at an acute angle. Upon completion of the gas piping, check for gas leakage.

When piping and connection parts are to be prepared on the user side, select clean ones with no oil and soil on the inner wall. Copper or stainless steel piping (1/8" O.D.) may be used. One half union for TOC-5000 air inlet (for 1/8" metal piping connection) is supplied as standard accessory.

Precautionary Requirements in Handling Gas Cylinder

Handling, maintenance and control of high pressure gas are regulated severely by the High Pressure Gas Regulation Act, general safety rules for high pressure gas and the Fire Services Act. Though gas used in this equipment is safe, a high pressure gas cylinder can be extremely dangerous if it is handled improperly. Be sure to observe the following points in handling a gas cylinder:

1) Install the cylinder in a well-ventilated place not exposed to direct sunlight.
2) Maintain the cylinder temperature not higher than 40°C. Do not use fire within 2 m range from the cylinder.
3) Fix the cylinder with rope so that it will not fall down.
4) Be sure to close the main cock of the cylinder immediately after completing supplying gas.
5) Inspect the pressure gauge for function at least once every three months.

2.8 Connection of Drain Piping

Drainage from cooler drain pot, from IC reaction vessel and from
the drain output of slidable sample injection ports for TC and IC
are collected in drain tube at the equipment right side. Connect
the drain tube with external drain tubing to lead drainage into an
appropriate drain container placed outside the equipment. (See
Fig. 1.1.) To make the resistance of the external drain tubing
as small as possible, place the end of the tubing in the atmosphere
near the equipment, and ensure that the tubing is placed at a lower
level than the drain port. Large resistance could hamper satisfac-
tory drainage, causing drainage to overflow inside the equipment.
Note that the drainage may contain acids.

Prepare a drain container on the user side. A polyethylene tank
of 10 to 20 ℓ capacity is suitable as a drain container. Alterna-
tively, if a drain pit is available near the equipment, drainage
may be discharged directly in the pit.

3. MEASURING PRINCIPLE

3.1 Measurement of TC (Total Carbon)

TC combustion tube is filled with oxidation catalyst and heated to 680°C. Carrier gas (high purity air) is supplied into this tube after it is controlled at a flow rate of 150 mℓ/min. by a pressure controller and a mass flow controller and moistened by a humidifier. When sample has been introduced by a sample injector into the TC combustion tube (100 $\mu\ell$ at the maximum for TC catalyst and 2,000 $\mu\ell$ at the maximum for high sensitivity TC catalyst), TC component in the sample combusted or decomposed to become CO_2. The carrier gas which contains combustion product from the TC combustion tube flows through an IC reaction vessel and cooled and dried by a dehumidifier. It is then sent through a halogen scrubber into a sample cell set in a non-dispersive infrared gas analyzer (NDIR) where CO_2 is detected. The NDIR outputs a detection signal (analog signal) which generates a peak whose area is calculated by a data processor.

The peak area is proportional to the TC concentration of the sample. Therefore, if calibration curve equation expressing the relation between peak area and TC concentration has been obtained in advance using TC standard solution, the TC concentration of the sample can be determined from the calculated peak area.

For reference, TC is composed of TOC (total organic carbon) and IC (inorganic carbon).

3.2 Measurement of IC (Inorganic Carbon)

Sample (2,000 $\mu\ell$ at the maximum) is introduced with a sample injector into an IC reactor vessel where carrier gas is flowing in form of tiny bubbles in the solution acidified by IC reagent. Only IC component in the sample is decomposed to become CO_2 which is detected by the NDIR. The IC concentration can be determined in the same procedure as the TC concentration.

Carbon in form of carbonates and hydrogen carbonates can be measured as IC.

3.3 Measurement of TOC (Total Organic Carbon)

TOC concentration can be obtained by subtracting the IC concentration calculated in the Para. 3.2 from the TC concentration calculated in the Para. 3.1.

3.4 Measurement of NPOC (Non-purgeable Organic Carbon)

TOC concentration can be obtained in a different procedure if sample has been acidified before it is set in the equipment. Specifically, the equipment sparges the acidified sample automatically with high purity air to eliminate IC component prior to measuring TC concentration. The measurement thus obtained is also generally called TOC, although it is named NPOC here to be distinguished from TOC obtained by the procedure in the Para. 3.3. NPOC stands for non-purgeable organic carbon and refers to non-volatile organic carbon. It particularly indicates non-volatile organic carbon which will not be eliminated by evaporation during sparging process; since volatile organic substance such as organic solvent which may be contained in sample is easy to evaporate at an ordinary temperature, it is possibly eliminated during sparging process. Organic carbon which is evaporated during sparging process is called POC (purgeable organic carbon).

NPOC is identical with TOC obtained by the acidic sparging process described in the TOC-related standard methods and referred to in water qualtiy-related test methods.

3.5 Electric Signal Processing

Amplifier of NDIR outputs analog signal corresponding to CO_2 concentration in carrier gas. The signal is input to V/F converter and converted to pulse frequency proportional to the input signal. The pulse signal insulated by photo coupler is read in CPU which detects peaks, measures the peak area and outputs the result to LCD and/or printer.

3.6 Peak Area Measurement

CPU detects starting and ending points of peaks generated by sample injection and calculates peak area automatically. Peak gradient (slope of tangential line at every moment) is used for this detection. CPU identifies peak starting point when positive peak gradient exceeds a specified value, and peak ending point when negative peak gradient becomes smaller than a specified value. When large amount of sample is injected for TC measurement, two peaks are generated overlapping or close to each other. In such a case, CPU detects the ending point of the latter peak alone and outputs the total area of the two peaks to the printer. Even for a peak with fluctuating base line, accurate peak area calculation is performed by base line correction. (See Fig. 3.1.)

On detecting peak ending point, the peak area is displayed on LCD. Occasionally, CPU cannot detect peak ending point within a specified period of time (within about 4.5 m minutes for TC and about 3.5 minutes for IC after sample injection) after detection of peak starting point. In such a case, the area of peak generated by that specified time is displayed with a latter T on the right side.

If sample does generate a peak, the peak will rise within 1.5 minutes from sample injection. Therefore, when CPU does not detect peak starting point within this period, it judges that no peak will be generated. Then, 0 is displayed for peak area.

On 「DATA PROCESSING」 screen, peak is displayed all through the period from sample injection (when INJECTING is displayed) until calculated peak area is displayed (at the end of MEASURING), and auto zero function works for all the other period.
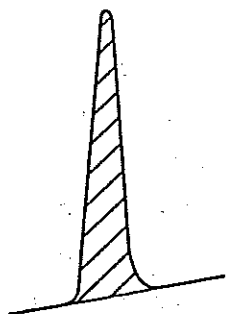
Peak area processing
for fluctuating base
line
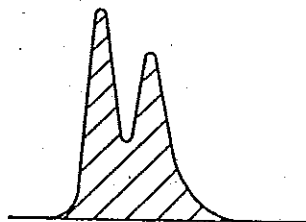
Peak area processing
for multiple peaks

Fig. 3.1 Peak Area Processing Method

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3.7 Calibration Curve

The equipment has the following functions for developing calibration curves.

3.7.1 One point calibration curve

Output signal of NDIR is linearized for all ranges. Neither TC combustion system nor IC reaction system provides factors causing the concentration-output characteristic to be deviated from linearity. Therefore, one or two point calibration curve is satisfactory enough to obtain measurement.

For IC calibration curve or TC calibration curve of a relatively high concentration (generally 100 mg/ℓ or higher) which passes the origin or a point near the origin, one point calibration curve can be used with no problem.

When sample is analyzed with standard solution concentration set for 1st STD CONC on 「CALIBRATION/CONDITIONS」 screen, CPU judges that the calibration curve passes the origin.

3.7.2 Multi-point calibration curve

For more reliable measurement, multi-point (up to four points) calibration curve may be used.

For three or four point calibration curve, a polygonal calibration curve or a linear regression calibration curve using the least-squares method is generated.

3.7.3 Shifting to origin

Shift-to-origin operation on 「CALIBRATION CURVE」 screen permits parallel shift of a calibration curve which does not pass the origin.

This function is useful when TC content in water used in preparing standard solution is too large to ignore with respect to the standard solution concentration (or when a calibration curve is to be developed using standard solution of concentration normally not higher than 10 mg/ℓ). That is, this function is used in developing a calibration curve for which correction is made for the TC component contained in the water.

For instance, if two point calibration curve is developed using standard solution with TC content of 10 mg/ℓ (actually $10 + \alpha$ mg/ℓ) prepared with water containing α mg/ℓ of TC, calibration curve as

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indicated by solid line in Fig. 3.2 is obtained. If this calibration curve were used directly, measurement would be always lower by α mg/ℓ than the actual value. If the calibration curve is shifted by the shift-to-origin function as shown by dot line in Fig. 3.2, it is possible to compensate the calibration curve deviation caused by α mg/ℓ of TC component contained in water used in preparing the standard solution.

However, when there is system blank caused by TOC meter, this method will yield measurement higher by the corresponding value than the actual value. In most cases, however, since measurement error by TC content in water used in preparing standard solution is much greater than the system blank, satisfactory measurement can be attained by correcting the error by TC content. If system blank provides any problem, conduct TC blank checking following the instruction shown in Para. 6.5. System blank can be compensated by subtracting the blank peak area from sample peak area.
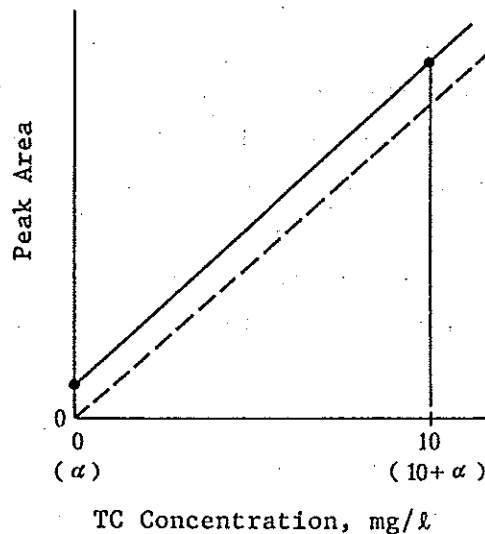
Fig. 3.2 Shifting Calibration Curve to Origin

3.7.4 Sparging process in measurement of standard solution

SPARGE TIME can be set at the time of setting condition for TC calibration curve on 「CALIBRATION/CONDITIONS」 screen. If the equipment is started with this parameter set and with sparge tube connected to the standard solution line, standard solution is sparged with carrier gas for a period of set time prior to measurement.

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This function is useful when concentration of TC standard solution used is so low that carbon content in dissolved CO_2 in the standard solution gives influence on the concentration. Specifically, dissolved CO_2 is eliminated by sparging process. Concentration of dissolved CO_2 in water used for preparing standard solution depends on water purification process, water storing method if it has been stored and CO_2 content in the atmosphere. In addition, if water itself contains only a small amount of dissolved CO_2, it can contact with the atmosphere and CO_2 may be dissolved during the standard solution preparing process. For reference, the amount of CO_2 dissolved from the atmosphere into water is shown in Table 3.1. In any case, key factors in determining whether or not this function is to be used are the concentration of standard solution to be used and that of TOC contained as impurity in water. This function is supposed to be used when the amount of TOC contained as impurity in water is negligibly small but the amount of dissolved CO_2 in water is large enough to have influence on the standard solution concentration. When this function is used, process of shifting calibration curve to the origin is not necessary. Sparging operation is not needed if shift-to-origin function is to be used. By this sparging function, system blank of the equipment can be compensated, although measurement obtained is lower than the actual value by TOC content as impurity in water. Do not sparge IC standard solution; IC concentration would be decreased by sparging.

3.7.5 Storage and reading of calibration curve

The equipment is capable of storing up to 18 calibration curves developed.

In setting conditions for calibration curve on 「CALIBRATION／CONDITIONS」, the first condition to be input is calibration curve No. (CAL CURVE F#, Number from #1 to #18 can be input). When setting the number, refer to the current file state of the calibration curves #1 through #18 displayed at ≪CALIBRATION FILE STATUS≫ in the lower right part on the screen. Any number with indication of FREE or STORED can be designated. When a calibration curve is generated after designating an appropriate number, the calibration curve is stored under the designated number. FREE indicates that the number

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is open whereas STORED indicates that a calibration curve has been
stored under the number. Accordingly, if a new calibration curve
is stored under the STORED number, the old calibration curve will
be replaced by the new one. To prevent this replacement, conduct
protect operation on the 『CALIBRATION CURVE』 screen. Then, PROTECT
is displayed for the number at «CALIBRATION FILE STATUS», and the
number cannot be designated when setting conditions for calibration
curve.

Calibration curves already stored can be listed on 『CALIBRATION CURVE
FILE LIST』 screen. Detail of each calibration curve can be examined
on 『CALIBRATION CURVE』 screen.

Delete a calibration curve file on 『CALIBRATION CURVE FILE LIST』
when it is no more necessary.

Any calibration curve stored can be called onto the screen by in-
putting the corresponding number at CAL CURVE # when measuring
condition is set on 『SAMPLE MEASUREMENT／CONDITIONS』 screen.

For analysis with this equipment, it is essential to develop a
calibration curve with standard solution for each measurement.
When stored calibration curve developed for previous measurement
is used, it should be kept in mind that resultant measurement
can contain error caused by sensitivity change during the storage
period and by inadequate setting of carrier gas flow rate.

Table 3.1 CO_2 Content in Distilled Water Equilibrated
with Atmosphere (mg/ℓ)

CO_2 Content in Atmosphere (vol%) / Temperature (°C)	0	5	10	15	20	25	30
0.030	1.00	0.83	0.79	0.59	0.51	0.44	0.38
0.033	1.10	0.91	0.76	0.65	0.56	0.48	0.42
0.044	1.47	1.22	1.02	0.87	0.74	0.64	0.56

$$CO_2 \ (mg／ℓ) \times 0.27 = C \ (mg／ℓ)$$

3.8 Quantitative Calculation

Measured concentration of sample is obtained by quantitative cal-
culation based on the measured peak area using the calibration
curve developed in advance.

It is displayed in any unit selected from among ppm, ppb, mg/ℓ
and μg/ℓ on 「GENERAL CONDITIONS」 screen for setting general analysis
conditions.

3.9 Calculation of Mean Value, Standard Deviation and Coefficient
     of Variation

In either measurement of standard solution in CALIBRATION mode or
measurement of sample in SAMPLE MEASUREMENT mode, if sample is
injected two or more times for repetitive measurement, mean value
(MN), standard deviation (SD) and coefficient of variation (CV)
are calculated and displayed on the screen.

SD and CV are used to check for the repeatability (fluctuation in
measured values for an identical sample in repetitive measurement).
The maximum number of sample injections allowed for the initial
setting is 10. Since three more injections can be added, up to 13
times of injections are possible.

3.10 Deletion of Measured Value and Additional Measurement

As standard solution or sample is measured repetitively, measure-
ments obtained may contain abnormal values. Such abnormal values
can be deleted or restored by key operation. After deleting abnor-
mal values, MN, SD and CV are calculated automatically and displayed
again.

Additional measurement is also possible. Detail of operation for
additional measurement is found in the paragraphs of 「DATA PROCESSING
STANDARD」 (P. 81) and 「DATA PROCESSING SAMPLE」 (P. 92) of Para. 6.3.

3.11 Automatic Measurement to Replace Abnormal Value

When measured values obtained in repetitive measurement have large
fluctuation (with large SD and CV), additional measurement can be
conducted automatically to delete abnormal values (doubtful values

quite different from the rest) and perform calculations again.
This function can be operated in the following procedure:

(1) On 「CALIBRATION/CONDITIONS」 or 「SAMPLE MEASUREMENT/CONDITIONS」
    screen for setting measuring conditions, input a larger number
    for MAX NO OF INJ (maximum number of sample injections) than
    for NO OF INJ (number of sample injections). This difference
    in the number is the number of times of additional measurement.
    Therefore, this function will not work if the same number has
    been set for these parameters.

(2) SD and CV will be displayed under MAX NO OF INJ. Set SD and CV
    at values appropriate for the required repeatability.

(3) If SD or CV of measured values obtained through n times of
    sample injections is smaller than SC or CV setting, the mean
    value of the measured values is employed.
    If both exceed the settings, one more measurement is conducted,
    and SD is calculated for all combinations of n measured values
    selected from n+1 measured values to identify a combination
    for which SC becomes minimum. Then for the selected combina-
    tion, the same judgement is made on the SD and CV. If either
    SD or CV is smaller than the SD or CV setting, the mean value
    of this combination is employed as measured value. If not,
    another measurement is carried out. The above process will be
    repeated to obtain an adequate mean value until the number of
    sample injections becomes equal to the maximum number of sample
    injections.
    If either SD or CV cannot be made smaller than the setting in
    the above process, no further measurement is added, and mean
    value of a combination of n measured values which provides the
    smallest SD will be employed as measurement.
    Normally, repeatability is judged on the basis of CV alone.
    For the TOC-5000, both SD and CV are used for this judgement
    for the following reason.
    When carbon content of sample is small with respect to the
    measuring range, the resultant measurement tends to have large
    CV. Therefore, if CV alone were set, the equipment could not
    analyze sample whose concentration is low with respect to the
    measuring range. In order to enable the analysis, it would

be necessary to set CV at a larger value for sample whose concentration is appropriate for the measuring range setting. In contrast, if SD is included as criterion, it is possible to set CV at an adequate value for sample of appropriate concentration. In addition, even when sample concentration is extremely low, the number of injections for repetitive measurement need not be increased unnecessarily.

To the right of the space for setting SD and CV, reference values are shown in parentheses. Since repeatability can vary depending upon the carbon content, measuring range, injection volume as well as various conditions of the equipment, input appropriate values depending on the case.

Repeatability may be deteriorated due to influence by suspended solids (SS) and coexisting components particularly when sample is measured. Therefore, excessively strict SD and CV settings would require increased number of additional measurements, resulting in longer analysis time.

3.12 Measurement Correction by Dilution Factor

When diluted sample is to be measured, set dilution factor (DIL FACTOR) in advance on 「SAMPLE MEASUREMENT/CONDITIONS」 screen. Then, measurement is corrected by the dilution factor so that the concentration of the undiluted original sample (COR CONC) is displayed as measurement result on 「DATA PROCESSING SAMPLE」 screen. On 「DATA REPORT」 screen, measurements corrected by the dilution factor are displayed with indication of correction by dilution factor in the RMK (REMARK) column.

3.13 Automatic Setting of Measuring Condition

When concentration of standard solution has been set on 「CALIBRATION/CONDITIONS」 screen, the CPU will determine and show the measuring condition (range and injection volume) most suitable for its measurement on the display. Specifically, among a number of possible range/injection volume combinations which will result in the peak height of 70 to 90% (or in some cases 50 to 95%) F.S, the CPU will automatically select a combination with the smallest possible

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injection volume that secures sufficient repeatability; injection volume should be as small as possible to ensure longer life of TC catalyst and IC reagent. For the standard solution concentration of TC 200 ppm (250 microliter syringe is used.), for instance, peak height is almost the same at about 70 to 90% F.S when measurement is conducted under the condition of, say, range × 1 with 3 $\mu\ell$ of injection volume, range × 5 with 13 $\mu\ell$ of injection volume or range × 30 with 80 $\mu\ell$ of injection volume (although peak height tends to somewhat decrease with increase of injection volume). However, since 3 $\mu\ell$ is smaller than the minimum possible injection volume, the latter two conditions are selectable. Because of the smaller injection volume, the CPU will select range × 5 with 13 $\mu\ell$ of injection volume. The measuring condition thus set automatically can be changed later. As injection is repeated, foreign substance may stick to the injection needle point, resulting in increase in splashing sample. Such change in the injection way has larger influence on the measurement result (normally in form of larger higher CV) as the injection volume setting is smaller. In such a case, therefore, injection volume should be increased by setting the range larger. Specifically, of the combinations mentioned above as an example, the condition of range × 30 with 80 $\mu\ell$ of injection volume should be selected. Anyway, in changing the automatically set measuring condition, it is necessary to select injection volume-to-range ratio (injection volume/range) which is almost the same as that of the automatically set condition.

If two or more standard solution concentrations have been set for developing a multi-point calibration curve, the measuring condition will be set automatically for the highest concentration.

This function has been set on the basis of the height of peaks generated by TC standard solution using n-propyl alcohol which produces relatively sharp peaks. With standard solution using potassium hydrogen phthalate, generated peak height may be lower than the range specified above, which is of no problem in measurement. (See Para. 5.1.12.)

3.14 Automatic Change of Range and Injection Volume

If AUTO RANGING AND INJ VOL is set ON on 「GENERAL CONDITIONS」 screen, this function works at the time of sample measurement.

3.14.1 Automatic change of range

If sample cannot be measured with the initially set range, the range is changed at first. That is, if peak height exceeds the full scale (H is displayed in the RMK column of measurement result.) by the first sample injection, the range is changed automatically for higher concentration and measurement is conducted again. Supposing the initial range setting is ×1, for instance, the setting is changed to ×5. If the initial setting is ×30, since there is no higher range, the CPU does not change the range setting but proceeds to the step of the Para. 3.14.2.

If measurement can be conducted within the full scale of the new range setting, sample is injected the specified number of times for measurement, and the new range setting is displayed in the RMK column. Quantitative calculation result (concentration) is displayed after it is corrected using the ratio of the new range setting to the old one. For example, if ×1 has been changed to ×5, peak area measured with the ×5 range is applied to the calibration curve developed with the ×1 range to obtain the concentration, and the concentration multiplied of five is displayed.

If peak height still exceeds the full scale with the new range and if there is higher range to be set, the range setting is changed again for higher concentration. The initial setting of ×1 can be thus changed to ×30 at the maximum. That is, sample of concentration 30 times as high as the initial setting can be analyzed.

3.14.2 Automatic change of injection volume

Peak height may exceed the full scale even with ×30 range. In such a case, the initial injection volume setting is changed as a rule by a factor of either 1/2 or 1/5. (In special case, injection volume is changed by 1/2.5.) Appropriate change ratio is selected automatically according to the state in which the peak height exceeds the full scale. If 1/2 or 1/5 of the initial setting is not an integer, the fraction is rounded off to an integer. For 1/2 of 35 μℓ, for example, new setting is 18 μℓ (17.5 μℓ is rounded off). Measurement with the new injection volume setting is corrected using the ratio of the new setting to the old setting, and the new injection volume setting is displayed on the RMK column.

The following points must be further noted for these functions (3.14.1 and 3.14.2):

· The range change ratio and injection volume change ratio with this function contain error of several % order. It must be noted that this error can become more serious particularly when change ratio is large, when injection volume is small (for example, in case injection volume is changed from 8 μℓ to 4 μℓ), or when both range and injection volume are changed. For accurate measurement of sample of wide concentration range, it is recommended to utilize the "automatic selection of optimum calibration curve" function.

· "Automatic change of range and injection volume" function and "automatic selection of optimum calibration curve" function can be operated in combination. The latter function takes precedence of the former function. If measurement cannot be conducted with change by the "automatic selection of optimum calibration curve" function, the "automatic change of range and injection volume" function works.

· The "automatic change of range and injection volume" function does not work for enlarging small peaks (that is, for higher sensitivity range or larger injection volume).

· When the "automatic change of range and injection volume" function has worked during measurement, indication of that fact is shown in the RMK column when measurement result is displayed on 「DATA REPORT」 screen.

3.15 Automatic Selection of Optimum Calibration Curve

When setting sample measuring condition on 「SAMPLE MEASUREMENT/ CONDITIONS」 screen, up to three calibration curves can be designated. The "automatic selection of optimum calibration curve" function works when two or three calibration curves have been designated. This function works as follows:

(1) Measurement is conducted first with the first calibration curve (1st CAL CURVE abbreviated as STD#1 here.)

(2) If sample measurement value (SAMP) is smaller than the maximum concentration (hereinafter referred to simply as concentration) of the first calibration curve and larger than the concentration of other calibration curves (STD others), the first calibration curve is used.

STD#1 > SAMP > STD others → STD#1 is used.

(3) If sample measurement value (SAMP) is smaller than the concentration of the other calibration curve which is smaller than that of the first calibration curve, then, the other calibration curve is used.

STD#1 > STD other > SAMP → STD other is used.

If three calibration curves have been designated, the function works as follows:

STD#1 > STD other 1 > SAMP > STD other 2 → STD other 1 is used.
STD#1 > STD other 1 > STD other 2 > SAMP → STD other 2 is used.

(4) If sample measurement value is larger than the concentration of the first calibration curve and the other calibration curve has higher concentration than the first calibration curve, the function works as follows:

① When sample measurement value has H mark (indicating that peak height exceeds the full scale of the range of the first calibration curve), the other calibration curve is used.

STD other > SAMP ⒣ > STD#1 → STD other is used.

② When sample measurement value does not have H mark, the CPU compares the ratio of the measurement value to the concentration of the first calibration curve with that to the concentration of the other calibration curve so as to determine the appropriate calibration curve. Mostly, the first calibration curve is selected because of the following reason: With any range setting, the NDIR output is linear in the range. Besides, if the "automatic setting of measuring condition" function is used, sample measurement value without H mark never exceeds the concentration of the first

calibration curve in large amount. Therefore, even in a range exceeding the concentration of the first calibration curve, quantitative value obtained by extending the first calibration curve is fairly accurate and almost the same as that obtained with other calibration curves.

STD other > SAMP > STD#1 → In most cases, STD#1 is used.

③ If sample measurement value is larger than the concentration of the other calibration curve, the other calibration curve is used.

SAMP > STD other > STD#1 → STD other is used.

(5) If sample measurement value is larger than the concentration of the first calibration curve and the other two calibration curves have higher concentration than the first calibration curve, measurement is conducted first with a calibration curve with the lower concentration prior to the process described in (4) above.

STD other 1 > SAMP > STD other 2 > STD#1
   → In most cases, STD other 2 is used.
SAMP > STD other 1 > STD other 2 > STD#1
   → STD other 1 is used.

The following points must be further noted for this function:

· The process by the CPU is the same as above if multi-point calibration curve is contained. (There is no particular process for multi-point calibration curve.)

· In repetitive measurement, the CPU makes judgment for the above process on the basis of the measurement by the first sample injection. In the (4) ② step, for instance, if H mark is shown for the measurement value by the second or subsequent injection, the equipment will continue operating on the basis of the measurement by the first sample injection. H mark is shown for some measurement values and not for others because of fluctuation in the repetitive measurement with peak height close to the full scale of the range.

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Therefore, if some measured values have H mark, the excess of the peak height of the full scale is too small to affect the measurement.

· The TC catalyst type (NORMAL SENS or HIGH SENS) and the microliter syringe size used for obtaining the 1st through 3rd calibration curves must be the same as those of the general condition settings.

Different unit may be used for the concentration of each calibration curve if it is of the identical unit group. When various units are used, calculation is necessary for conversion between the units.

For example, ppm and ppb are in the same group and mg/ℓ and µg/ℓ are in the same group. Calibration curve developed in the unit of ppm is compatible with the one in the unit of ppb but not with the one in the unit of mg/ℓ. The unit of concentration need not conform to that of the general measuring condition setting. (The unit of concentration for calibration curve takes precedence of that of the general condition setting.)

· To make effective use of this function for measurement of wider concentration range, it is recommended to set the concentration ratio between two calibration curves at 5 to 10.

Considering that measurement is always started with the 1st calibration curve, a calibration curve which is most often used should be allocated as the first calibration curve. The priority of the 2nd or 3rd calibration curve depends on the concentration setting of each calibration curve and the sample concentration.

· This function cannot be used with the of "quantification by carbon content" function as described below.

3.16 Quantification by Carbon Content

Quantitative calculation by comparison with calibration curves uses concentration. In this context, sample injection volume for sample measurement must be the same as that used in developing calibration curves.

Quantification is also possible by comparing carbon contents because peak area is proportional to the carbon content in sample, and co-existing components such as water give relatively small influence (matrix effect) on the peak area.

Carbon content is obtained as a product of the concentration and the injection volume. For instance, the carbon content in 10 $\mu\ell$ of sample with TC 100 mg/ℓ is 100 mg/ℓ × 10 $\mu\ell$ × 10^{-6} × ($\ell/\mu\ell$) = 1 × 10^{-3} mg, and that in 50 $\mu\ell$ of sample with TC 20 mg/ℓ is 20 mg/ℓ × 50 $\mu\ell$ × 10^{-6} ($\ell/\mu\ell$) = 1 × 10^{-3} mg. Since the two samples contain the same amount of carbon, they produce peaks of almost the same area. (Actual measurement may contain error of several % order due to an inevitable error in injection volume and some influence by matrix effect.)

This function is useful in measuring a trace amount of TOC in, say, pure water. When preparing standard solution, TC in pure water used and carbon component entering the solution during preparation process affects the TC content in the standard solution. Therefore, if you intend to prepare standard solution with 1 mg/ℓ of TC, the actual standard solution obtained often contains dozens of % larger amount of TC, resulting in measurement error.

If the following operation is conducted with this function, unnecessarily great care need not be taken in preparing or handling standard solution and measurement error can be minimized because the standard solution of about 10 times as high TC concentration as necessary is used.

(1) Use high sensitivity TC catalyst and set 500 $\mu\ell$ microliter syringe.

(2) Prepare standard solution of TC 10 mg/ℓ. Set 1st STD CONC 10 (mg/ℓ) on 「CALIBRATION CURVE/CONDITIONS」 screen. Then develop a one-point calibration curve by normal measurement operation.

(3) Set the obtained calibration curve in 1st CAL CURVE # on 「SAMPLE MEASUREMENT/CONDITIONS」 screen. Change the sample injection volume shown on the screen by the "automatic setting of measuring condition" function (in this case, 53 μℓ) to 500 μℓ, and then measure sample.

(4) The 「DATA PROCESSING SAMPLE」 screen displays the measurement obtained by concentration comparison with TC 10 mg/ℓ first and finally the measurement corrected with the ratio of sample injection volume (500 μℓ/53 μℓ = 9.43 times) as COR CONC INJ. Even with this method, TC 10 mg/ℓ standard solution contains excessive carbon amount corresponding to the carbon content in water used in preparing the standard solution. For further correction, generate a two-point calibration curve setting 0 mg/ℓ for water used in preparation, and use SHIFT TO ORIGIN on 「CALIBRATION CURVE」 screen.

The following points must be noted for this function:

· Injection volume ratio must not be higher than 10.

· When the microliter syringe selected provides small stroke, large error results between the ratio of sample injection volume to standard solution injection volume setting and the corresponding ratio in the actual injection. Therefore, select a syringe which allows as large stroke as possible. For injection of 50 μℓ of standard solution and 500 μℓ of sample, for instance, 500 μℓ microliter syringe provides larger stroke than 2,500 μℓ syringe.

· Measure sample under the normal condition (that is, the same injection volume for standard solution and sample) as long as possible.