Measuring Air Pollution and the Protection of Cultural Properties in the Historic City of Nara, Japan

-Preparation and analysis of samples for air pollution study (laboratory training)-

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Summary

Nara is a famous historic city with many cultural heritage. The air pollutant levels in Nara are lower than in many other Japanese cities, but even this relatively low level of air pollutant affects many cultural properties. For example, in recent years the Todaiji temple's Hakkaku Toro (bronze lantern, 8th century) has corroded conspicuously and the Chogakuji temple's Sekito (tuff pagoda) has also been damaged.

Nara University Conservation Science Laboratory have been measuring air pollutant at 12 locations outside and at 7 locations inside historic buildings or museums by the simple method of using a triethanolamin〔2,2',2" -nitro-tri-ethanol, $N(CH_2CH_2OH)^3$=149〕cylindrical filter (TEA-CF) from 1989.

Details of this report are available. Please refer the report "Measuring Air Pollution and the Protection of Cultural Properties in the Historic City of Nara, Japan" in our e-learning text 2004 version.

Overview of air pollution study

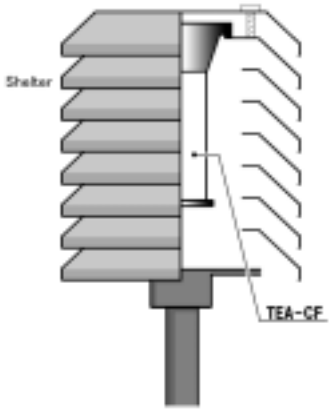
Simple concentration measurement of NO_2, SO_2 and CL by triethanol cylindrical filter method (hereinafter referred to as “TEA-CF method”). After exposing a cylindrical cellulose filter impregnated with 29.6% triethanol aqueous solution (hereinafter referred to as “TEA aqueous solution”) to the atmosphere for a period of one month, quantitative analysis is conducted by ion-exchange chromatography to cumulatively determine per month average concentration.

Quantitative values are converted to per day weight (μg/day/100cm^2: relative concentration), and are converted to absolute concentration (ppb) for NO_2 and SO_2. A 31-day continuous roll autographic recorder is provided at main measurement points to perform temperature offset for NO_2.

The measurement range for NO_2 is 1.9 μg of NO_2/day/100cm^2 and the range for SO_2 is 2.6 μg of SO_3/day/100cm^2.

Features of TEA

-Colorless liquid with minimal ammonia odor.
-Slightly viscous.
-Dissolves in water or ethanol.
-Heavier than water.
-Adsorbs to acidic gas.
-Comparatively low toxicity towards the human body.



1. Sample preparation

Required items

-2, 2', 2" nitro triethanol N ($CH_2 CH_2 OH_2$) = 149.19

-Cylindrical filter (ϕ3.3 mm x 100 mm, 103.7 cm^2 surface area, neutral)

-Ultra pure water

-Polyethylene cylinder (made by Kimoto Electric Co., Ltd., Japan)

Procedure

(1) Dilute the nitro triethanol (TEA) 3 times.

300ml of TEA + 600 ml of ultra pure water = 900 m of TEA solution

(2) Immerse the cylindrical filter in the TEA solution for 30 minutes.

(3) Remove the cylindrical filter from the TEA solution, stand it on the spread out acid-free filter paper and remove the excess water.

(4) Mount the filter on the cylinder.

-In addition to the samples for exposure, blanks for comparison or offset are also needed.

-The filters must not be touched with the bare hands.

-Ion exists in various places such as in the air, in people's bodies (surface of the skin, breath) and surface of apparatus. You must therefore be careful not to allow ion components to get mixed in when creating, extracting and preparing samples.

2. Preparations for analysis

Extraction and preparation of samples for analysis

Required items

-Tall beaker
-Hot plate
-Glass rod
-Suction filter apparatus
-Pipette (15 ml)
-Flat-bottom flask (200 ml)
-Measuring pipette (1 ml)
-Test tube (25 ml)
-Hydrogen peroxide (highest quality) (H_2O_2 = 34.01)

Procedure

(1) Divide the recovered TEA-CF into the proper size (about 8 – 16 divisions), place into a tall beaker and add 100 ml of ultra pure water. (The TEA-CF must not be touched with bare hands.)

(2) Place the tall beaker on a hot plate heated to approximately 120°C and heat for about an hour.

(3) After heating, crush the filter paper finely with a glass rod and suction filter.

(4) Bring the volume of the filtered liquid to 200 ml by adding the required amount of ultra pure water and agitate well (put a stopper in the flask, turn it upside-down and shake).→*This serves as the test solution.*

(5) Using a pipette, place 15 ml of the test solution in a test tube.

(6) Add 0.3 ml of highest quality hydrogen peroxide.

(7) Bring the volume of the solution to 20 ml by adding the required amount of ultra pure water and agitate well (put a stopper in the flask, turn it upside-down and shake). →*This serves as the sample solution for analysis.*

3. Overview of the ion chromatograph analysis method

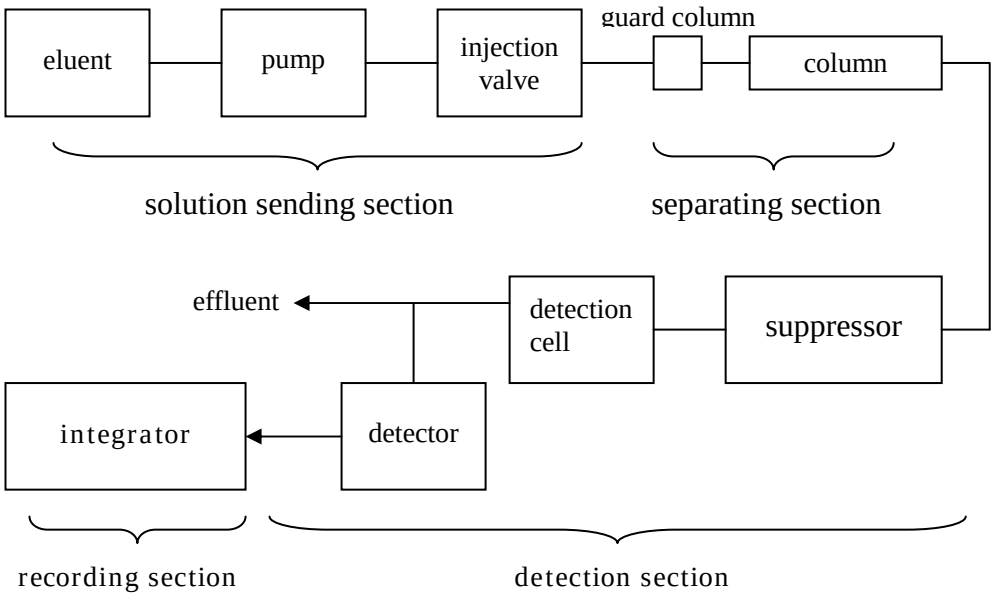
Features

-Type of ion-exchange chromatography

-Measures ion components contained in the aqueous solution sample. If the sample is a solid or a gas, measurement is made possible by converting the sample to an aqueous solution in preprocessing.

-Separate using a column filled with ion-exchange resin. Ion analysis can be accomplished by measuring ionic conductivity. High sensitivity analysis of ionic substances can be achieved by diminishing the background of the eluent using a suppressor.

Basic composition



(1) Solution sending section: Eluent bottle, pump, sample introduction section (injector and sampling board)

(2) Separating section: Guard column, analytical column

(3) Detection section: Suppressor, sensor

(4) Recording section: Pen recorder, integrator, computer, etc. (section that records the chromatogram)

4.Preparation of standard eluent

Anion analysis (Column: In case of IonPac AS4A-SC)

Required items

-Liquid concentrate A (0.18mol/L Na_2CO_3)

Na_2CO_3 19.08g + 1000ml of ultra pure water

-Liquid concentrate B (0.17mol/L $NaHCO_3$)

$NaHCO_3$ 14.28g + 1000ml of ultra pure water

-1000 ml flat-bottom flask (1)

-10 ml measuring pipettes (2)

-Small beakers (2)

Procedure

(1) Wash the flat-bottom flask with ultra pure water.

(2) Draw a small amount of liquid concentrate A and liquid concentrate B from the beakers.

(3) Using a measuring pipette, measure 10 ml of each and place it in the flat-bottom flask.

Before measuring, be sure to wash the measuring pipette with each solution. This is done to ensure an accurate constant volume. If any pure water used for washing remains inside the pipette, the solution will be diluted by the water. If it is dry, the solution may not flow smoothly along the walls of the pipette and make it impossible to accurately measure the amount.

(5) Introduce ultra pure water into the flask and bring the volume up to 1000 ml. This serves as eluent. *→eluent concentration: 1.8mmol/L Na_2CO_3 , : 1.7mmol/L $NaHCO_3$*

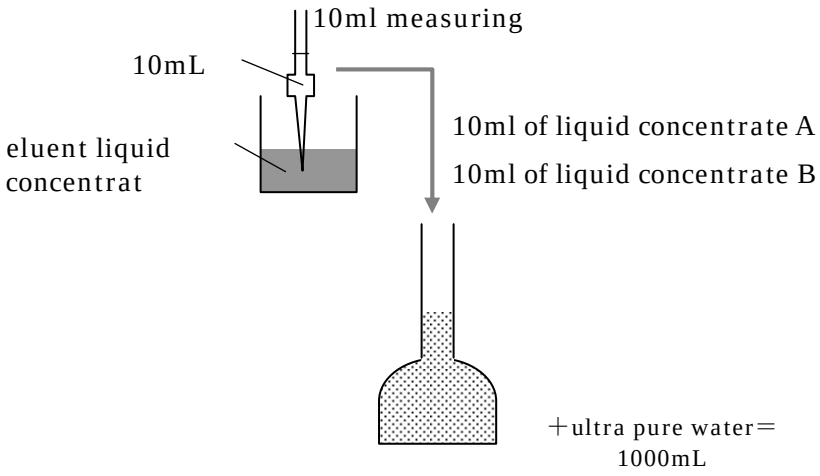
(6) Place eluent in a bottle for anionic eluent and allow the air in the solution to escape for about 5 minutes.

The tube that the sample passes through is extremely narrow. Air bubble in the solution may interfere and unable you to obtain a stable baseline and good peak line.

(7) After removing the air from the solution, mount the solution on an ion chromatography (hereinafter referred to as “IC”).

Take 10 ml of each liquid concentrate (A and B) for making eluent (stock solution) and bring the volume to 1000 ml by adding ultra pure water.

-2000 ml of eluent will be sufficient for each analysis.



(10ml of liquid concentrate A)+ (10ml of liquid concentrate B) + pure water = 1000 ml

-If tightly sealed, concentration of liquid concentrate for making eluent (stock solution) can be maintained for several months.

Cation analysis (Column: In case of IonPac CS4A-SC)

Required items

-methanesulfonic acid (2 mol/L methanesulfonic acid, Wako Pure Chemical Industries, Ltd., Japan)

-1000 ml flat-bottom flask (1)

-10 ml measuring pipettes (1)

-Take 10 ml of commercially available methanesulfonic acid (2 mol/l: Wako Pharmaceutical Co.), and add pure water to bring the volume to 1000 ml.

→*eluent concentration: 20 mmol/L of methanesulfonic acid*

10 ml of methanesulfonic acid + pure water = 1000 ml

Reference: Required amount of eluent**
Required amount of eluent in the hypothetical case assuming the analytic apparatus is operated from 4:00 pm of one day to 10:00 am of the next day (18 hours):

Anion: 1.5ml/min × 18 = 1620ml
Cation: 1.0ml/min × 18 = 1080ml

Max. operation time if eluent bottle is full (2-litter capacity)

Anion: 2000 ÷ 1.5ml/min = 22.2 hours
Cation: 2000 ÷ 1.0ml/min = 33.3 hours

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5. Preparation of standard sample (ST)

The following four types of standard sample (ST) are required. For ST1 – ST4, measure out the following amounts of commercially available mixed standard solution and bring the volume up to 100 ml with ultra pure water. Place the standard sample adjusted to a constant volume of 100 ml in a polyethylene bottle and store it in a refrigerator.

anion	cation	amount taken from commercially available product	dilution ratio
ST1	ST1	5ml	1/20
ST2	ST2	10ml	1/10
ST3	ST3	20ml	1/5
ST4	ST4	50ml	1/2

The ion concentration of commercial standard solution and in ST1 – ST4 after dilution are as follows:

Anionic mixed standard solution (IV)

Kanto Koatsu Kagaku Co., Ltd. (Cat. No. 01856-96) *Unit: mg/l (ppm)*

	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
Commercial ST	5	10	15	10	30	30	40
ST1	0.25	.5	.75	.5	1.5	1.5	2
ST2	0.5	1	1.5	1	3	3	4
ST3	1	2	3	2	6	6	8
ST4	2.5	5	7.5	5	15	15	20

Cationic mixed standard solution (II)

Kanto Koatsu Kagaku Co., Ltd. (Cat. No. 07197-96) *Unit: mg/l (ppm)*

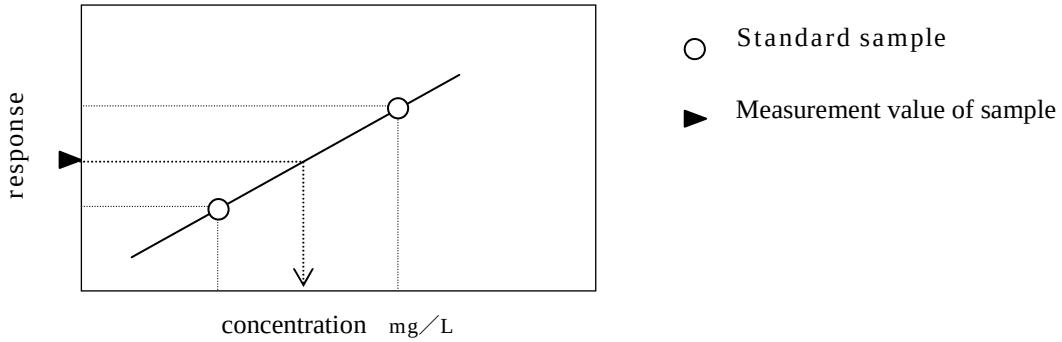
	Li^+	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
Commercial ST	0.5	2	2	5	5	5
ST1	0.025	0.1	0.1	0.25	0.25	0.25
ST2	0.05	0.2	0.2	0.5	0.5	0.5
ST3	0.1	0.4	0.4	1	1	1
ST4	0.25	1	1	2.5	2.5	2.5

Reference **********

Calibration line

After determining concentration of the objective component and relational expression of the response, concentration is calculated by matching the response obtained by measurement with the relational expression. The relational expression for this concentration and response is the calibration line.

Calibration line methods include the absolute calibration method (also called the



"external calibration method"), internal standard method and additional standard method. Suitable internal standard substances often cannot be obtained with ion chromatography, so the absolute calibration method is used under ordinary circumstances.

There are two types of calibration lines: the single point calibration line and multiple point calibration line. In either case, standard sample of a known concentration is analyzed. The concentration is plotted on the horizontal line and the response (peak are or height) is plotted on the vertical line. The concentration of measurement ion in the sample is determined by fitting to the relational expression for concentration and response value at that time.

Conversion formula in the TEA-CF method

Formula for conversion to relative concentration

CL^-＝ 257.15 * (CCL^- – B) ／ n　　unit: μgCL^-/day/100cm^2

NO_2＝ 257.15 * (CNO_2 – B) ／ n　　unit: μgNO_2/day/100cm^2

NO_3＝ 257.15 * (CNO_3 – B) ／ n　　unit: μgNO_3/day/100cm^2

SO_3＝ (CSO_3 – B) * 214.39 ／ n　　unit: μgSO_3/day/100cm^2

-CCL^-, CNO_2, CNO_3, CSO_3: Concentration of analysis results (μg/ml)

B: Concentration of blank

n: Number of days of exposure

Temperature offset

The concentration of NO_2 varies according to temperature. Temperature offset is executed using 20°C as the standard.

The difference in reaction is that whereas CL^- and SO_3 react with alkalis, NO_2 reacts chemically with the TEA impregnated in the sample.

$$C'_{TN} = C_{TN} \div T_{COR}$$
$$= C_{TN} \div (NR_T \div NR_{20})$$
$$= C_{TN} * NR_{20} \div NR_T$$
$$= C_{TN} * (0.12 * 20 + 4.5) \div (0.12 * T + 4.5) \quad \text{unit: } \mu g NO_2/day/100cm^2$$

- $-T_{COR}$: Offset coefficient using 20°C as the standard
- $-C'_{TN}$: NO_2 concentration by TEA-CF method of temperature offset
- $-C_{TN}$: NO_2 concentration by TEA-CF method
- -NR : NO_2 adsorption of TEA-CF 100 cm^2 per day
- -T : Temperature at each point

Formula for conversion to absolute concentration

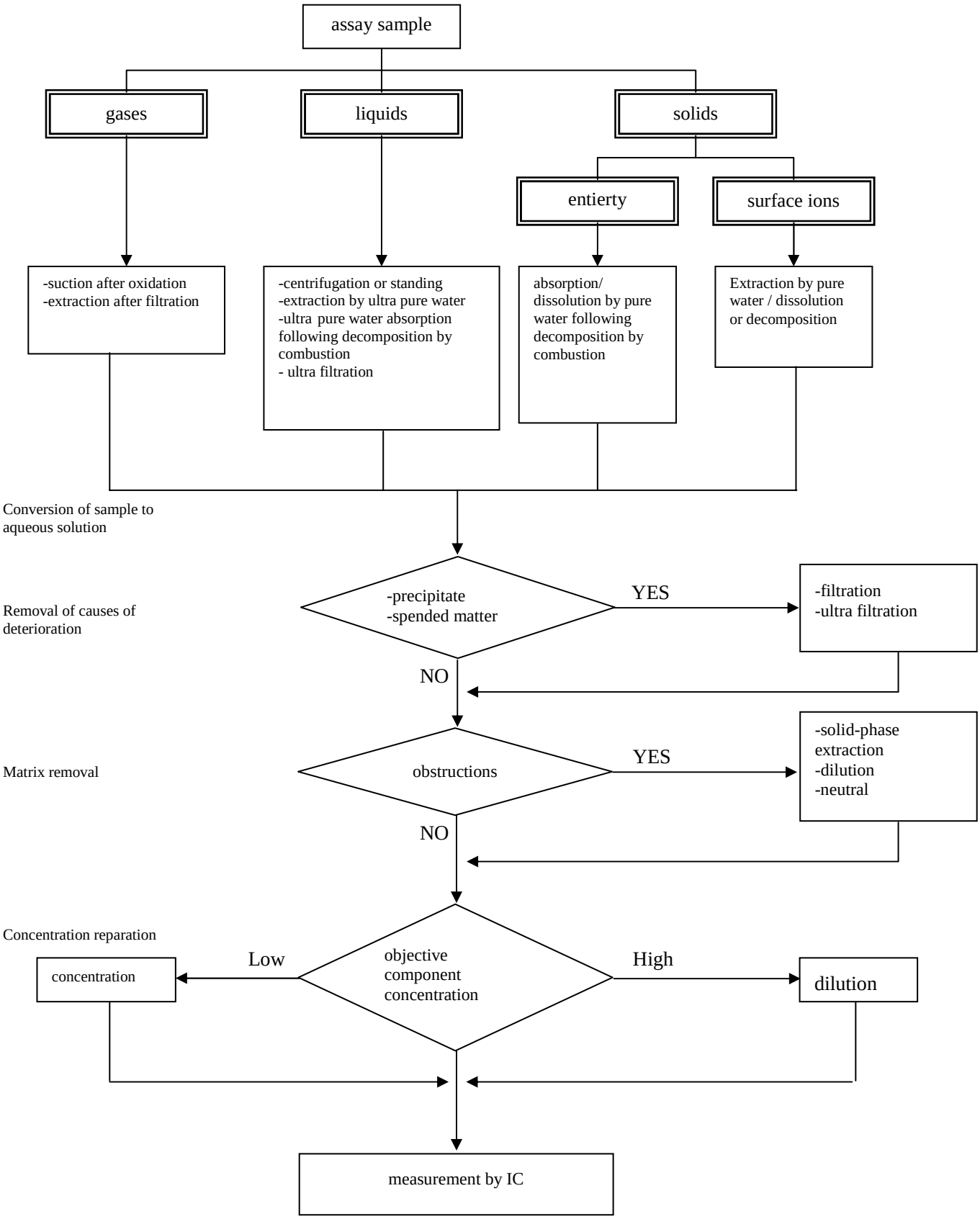
NO_2； $C_{AS} = 0.118 * C'_{TN} + 3.3$（ppb, 1 ppm = 1000ppb）

- $-C_{AS}$: NO_2 concentration (ppb) by automatic measurement instrument
- $-C'_{TN}$: NO_2 concentration by TEA-CF method of temperature offset

SO_2； $C_{AS} = 0.043 * C'_{TS} + 2.8$

- $-C_{AS}$: SO_2 concentration (ppb) by automatic measurement instrument
- $-C'_{TS}$: SO_3 concentration by TEA-CF method

Preprocessing flow



6. Analysis (at Nara University)

Equipment specifications and measurement conditions of Nara University Conservation Science Laboratory

■ DIONEX ICS-90、AS40

Measurement conditions

	Anion measurement	Cation measurement
Separation columns	IonPac AS4A-SC 4mm	IonPac CS12A
Guard columns	IonPac AG4A-SC 4mm	IonPac CG12A
Eluent	-1.8 mM sodium carbonate -1.7 mM sodium acid carbonate	20 mM methanesulfonic acid
Eluent flow	1.5mL／min	1.0mL／min
Sample injection	5 ml (using auto-sampler, 5 ml vial)	
Sample introduction	25 μL	25 μL
Suppressor	-ASRS 4mm electro dialysis -Anion auto-suppressor -Recycle mode	-CSRS 4mm electro dialysis -Cation auto- suppressor -Recycle mode

Specifications

Ion chromatograph ICS-90		
Injection valve		Rheodyne LLC, 1 unit (standard 25 μl loop)
Eluent solution pump	Type	Nonmetallic head, recypro-piston
	Liquid sending	Constant flow (w/mechanical damper)
	Flow	0.5～1.5 mL／min
	Max. pressure	21 Mpa
Electrical conductivity sensor	Type	Digital signal processing
	Range	0～500 μS
	Automatic offset range	0～999 μS
	Cell temperature setting	40°C (temperature control cell)
Controller		ICS-90 analyzer control / data processing
Installation temperature range		10～40°C
Dimensions (w/controller)		660（W）×400（D）×400（H） mm
Weight (w/controller)		Approx. 20 kg
Power source (w/controller)		100 V、50／60 Hz、7 A
Gas pressure		Accessory air pump

AS-40 auto-sampler	
Main unit	5 ml vial specs
Vial capacity	66 (11 cassettes)
Introduction speed	1 ml/min or 4 ml/min
Introduction count	Choice of 1, 2 or 3 times per vial
Wetted part material	Nonmetallic
Withstand pressure	0.69 Mpa（100psi）
Dimensions	368（W）×445（D）×302（H） mm
Weight	8.9 kg

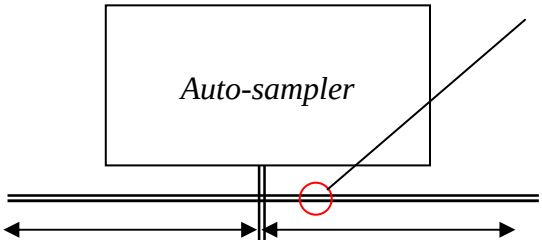
Program file settings

AS4A_CS12A_2.prg

	Anion measurement	Cation measurement
Eluent flow rate	1.5 mL／min	1.0 mL／min
Pump pressure	Low limit: 0 / High limit: 3000	
Import time	15 minutes	

-A new file may be created if needed, but the file is used as is under ordinary circumstances.

The “Anion_only.prg” is used if analyzing anions only.



If analyzing anions only, remove this part of the T joint and cap with a blind plug. The power of the auto-suppressor for cations must not be turned on.

The orange tube must be the same length for both the anion and cation sides.
(If the tubes are different lengths, the pressure will become unbalanced and the sample will not be introduced equally.)

Analysis procedure

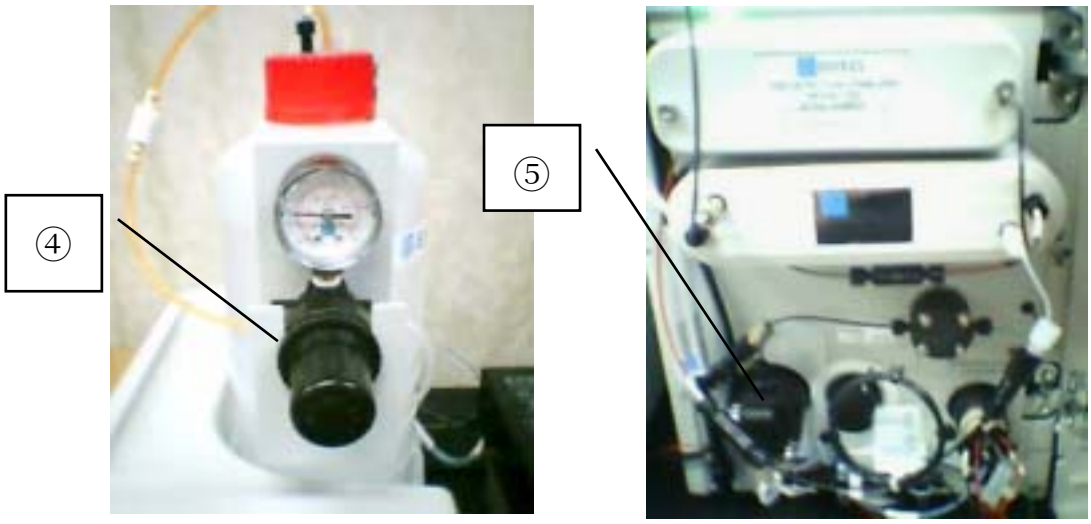
(1) Open the nitrogen valve. The nitrogen pressure should be 2.0 kg/cm^2

(2) Turn the power tap ON.

(3) Boot the computer.

(4) Adjust the eluent pressure (3 – 6 psi).

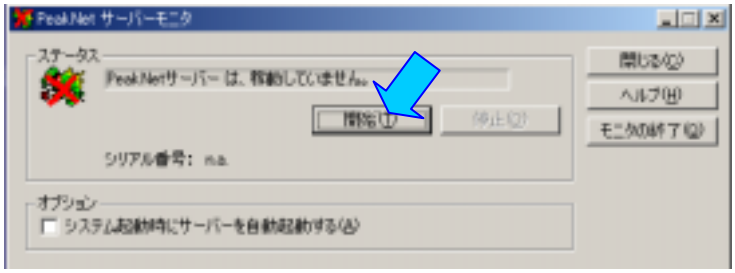
(5) Remove air.



When server monitoring is started, the IC is locked. You must therefore boot the IC first and then operate from the computer after starting the pump.

(6) Server monitoring start

1. Double-click the Server Monitor icon on the PC.
2. Click Start. Make sure the status changes to “Peak Net server is running in idle.”
3. Click Close.

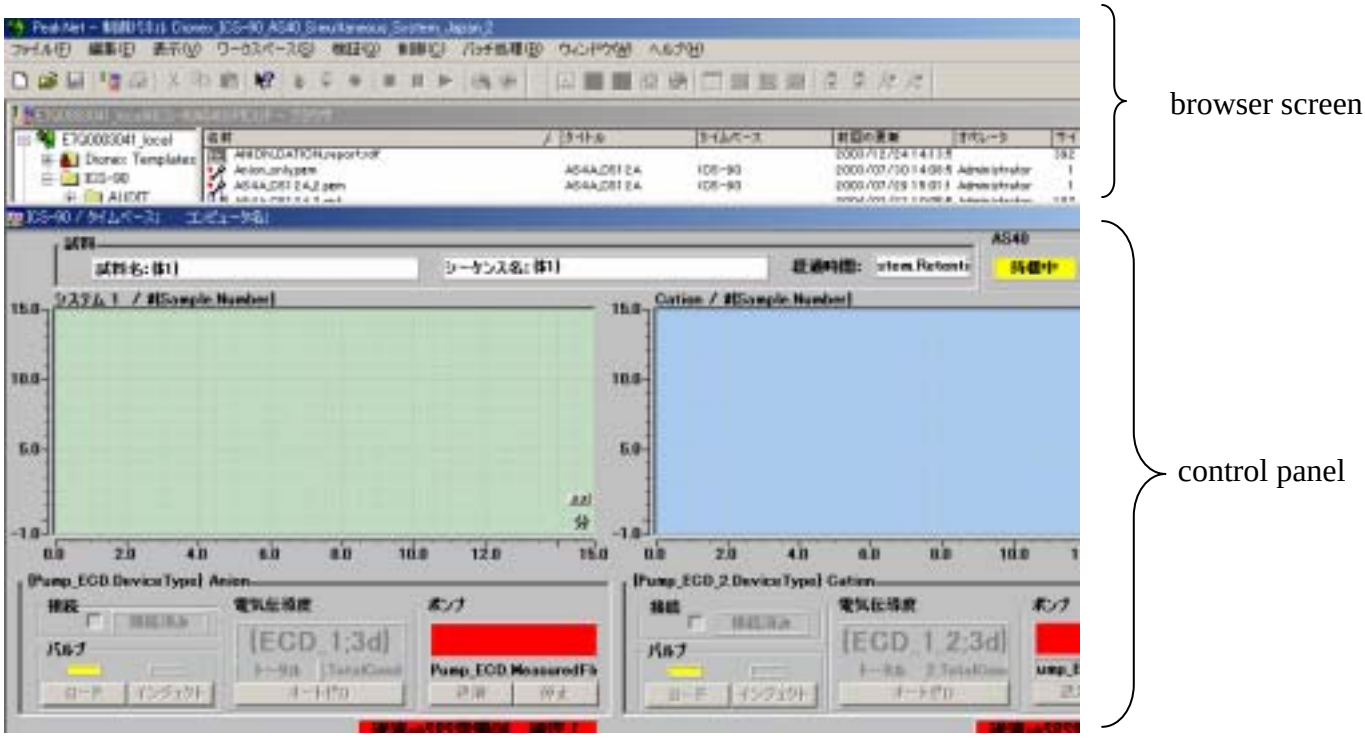


(7) Peak Net start

Double-click the Peak Net icon on the PC.

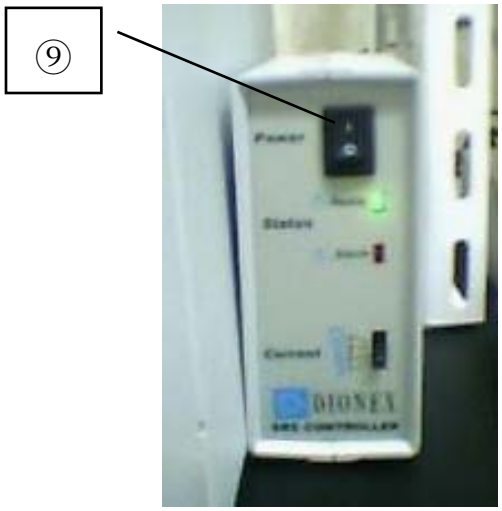
The control panel pops up in the front and the browser screen in the back.

If you remove the check from the Connect button on the control panel, the IC lock is canceled. ***Never remove the check during analysis.***



(8) Solution feed start

Click the Feed button on the control panel.



(9) Auto-suppressor power (external) ON

The current setting is 1 for anion and 2 for cation.

（1＝50mA、2＝100mA、3＝300mA、4＝500mA）

Eluent concentration is higher for cation so current is higher.

caution!

-Never turn the auto-suppressor's power ON when solution is not being pumped.

-Be sure to click the Feed button before turning the auto-suppressor's power ON.

-When you stop, be sure to turn the power OFF first, then click the Stop button.

(10) Baseline monitoring start

1. Click the Control and Import ON buttons on the control panel.
   (Make sure the there is a check in the checkbox for the two channels.) OK
   For anion analysis only, place a check in the checkbox of ECD_1 only.
   (Channel: ECD_1 = Anion, ECD_1_2 = Cation)
2. Click the Auto Zero button on the control panel.
   Wait until the baseline stabilizes (approx. 30 minutes).
   Target background electric conductivity (total): Anion = 12 – 15 μS
   Cation = 1μS or less

(11) Baseline monitoring stop

Click the Control and Import OFF buttons on the control panel.

(A message appears asking if you wan to stop monitoring now.) Click the Yes button.

To see the results of baseline monitoring, open the Manual import file in the MANUAK folder inside the ICS-90 folder on the browser screen. This file is automatically updated each time.

(12) Auto-sampler preparation

Press Hold/Run and wait till the green Ready lamp of Sampler lights.

To rinsing (pure water feed) prior to analysis, the status becomes Ready when rinsing

is finished.

(13) Analysis start

Prepare a sequence for analysis as described in the following section (Sequence setting).

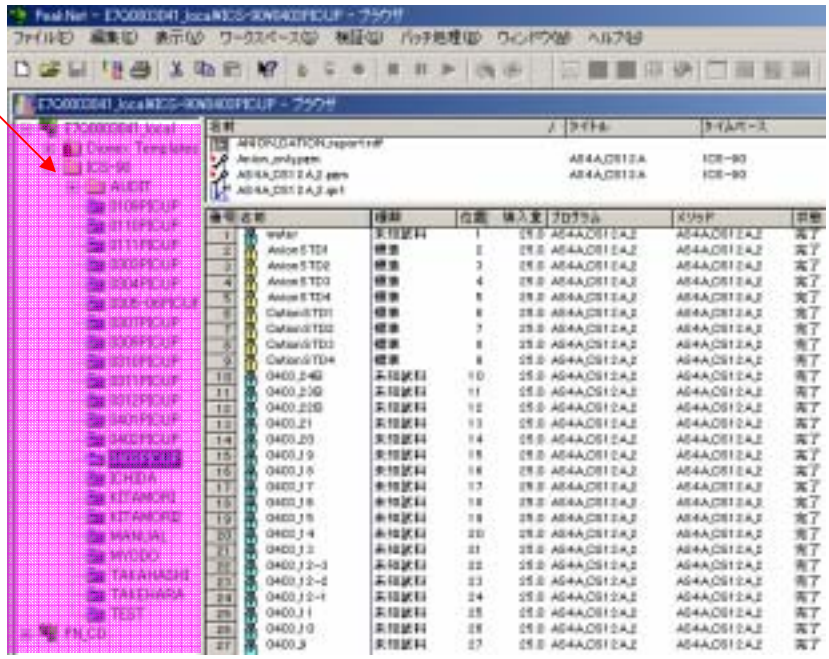
1. Open the sequence to be analyzed on the browser screen.
2. Batch processing – Start – Ready check
   (A message appears saying ready check was successful.) Start
3.Analysis then starts.

Sequence (analysis procedure schedule) setting

There are two methods of preparing a sequence: You can copy an existing sequence or prepare a new one from scratch using the wizard.

Method of copying an existing sequence (simple method)

Existing sequences are arranged in directory structure on the left side of the browser screen.



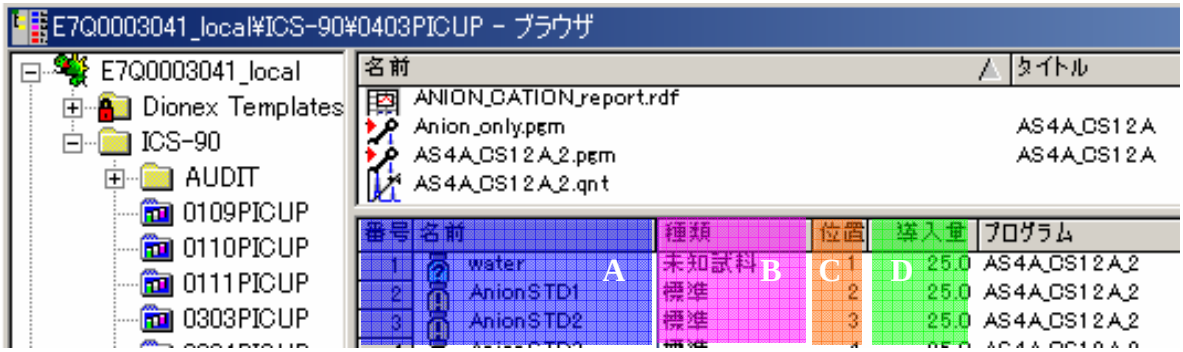
1. Select the sequence to be copied.
2. Click the File menu and then Save as.
   Type in a name for the sequence and click the Save button.
3. Select the sequence to be created.

Details concerning the files and sequences are displayed on the right side of the browser screen.

For the method of creating a sequence from scratch using the wizard, see the attached manual.

Sequence editing method

(For details, see the attached manual.)



A) Edit the sample name

Select the name to be changed, press the F2 key and type in the new name.

B) Edit the type of sample (standard, unknown, blank)

Click the right button of the mouse on the location of the type to be changed and select from the menu.

C) Position (auto-sampler vial position) editing

Click the position to be changed and type in the new information. You can also select the entire position column, click the right button of the mouse on it and select Edit file from the menu. You can then edit using the wizard.

D) Editing program to be applied (not changed under ordinary circumstances)

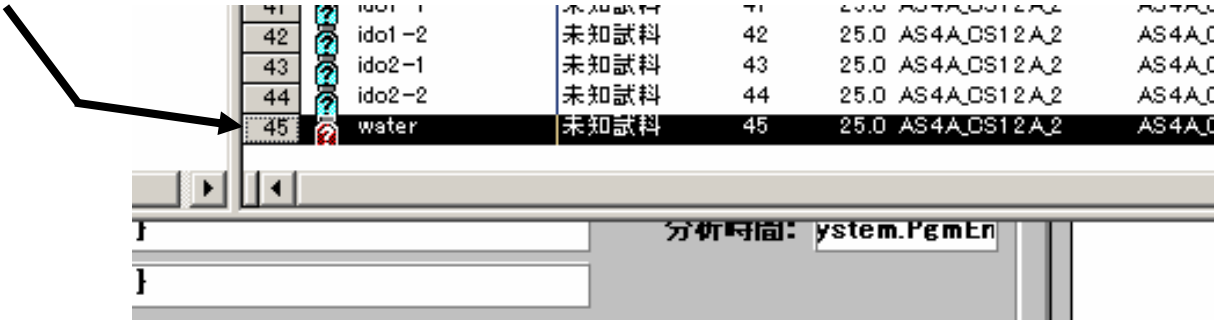
Click the right button of the mouse on the program to be changed and select from the menu.

You can add to the sequence line even while analysis is being carried out.

Line addition:

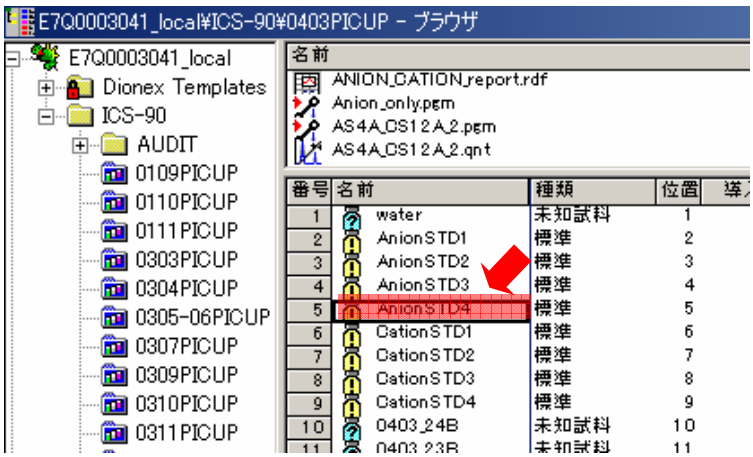
Select the last line and press the ↓key. If you want to insert a line, select the place

where you want to insert, click the right button of the mouse and select Add line from the menu.

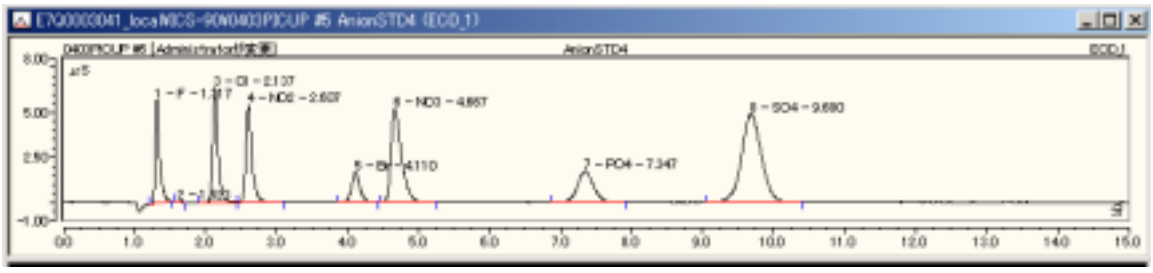


Calibration line creation(*Peak Net* analysis method)

(1) Check analysis results for standard sample (anion STD1 – 4, cation STD1 – 4)
Double-click the filename of the data you want to see in the browser screen.



example



Under ordinary circumstances, the cation chromatograph is displayed. Anion/cation channel switching (data display switch) is accomplished by the following icons:

Left side icon : *Displays anion*		*Right side icon:* *Displays cation*

Main check items

(A) Is the baseline proper?

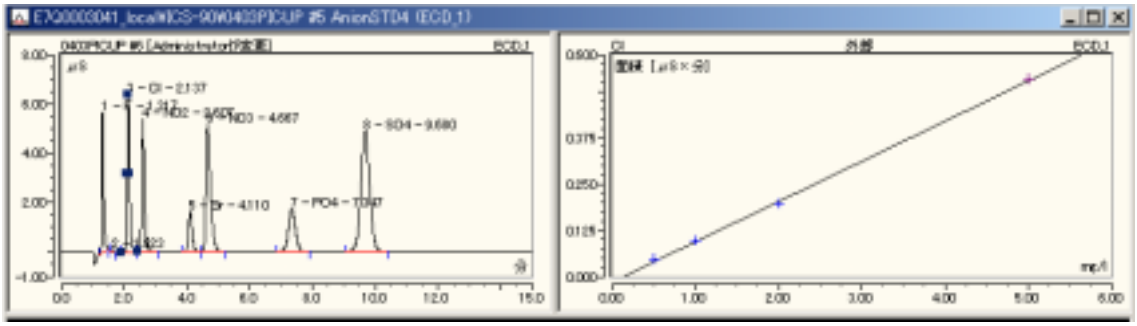
(B) Does each peak have a name?

Anion: F^-, Cl^-, NO^{2-}, Br^-, NO^{3-}, PO_4^{3-}, SO_4^{2-} (7 types)

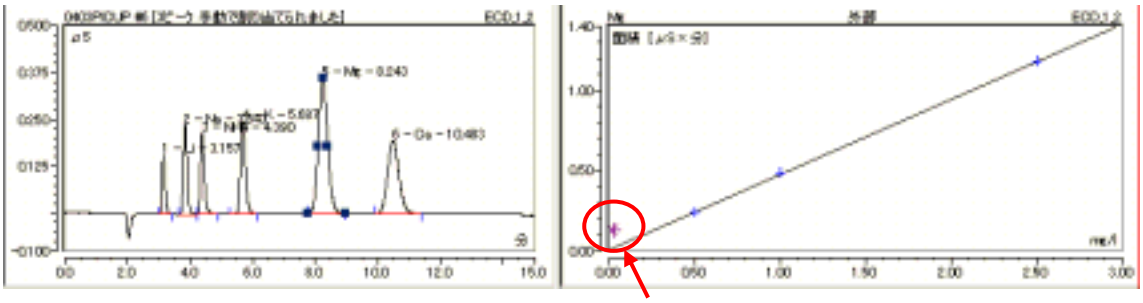
Cation: Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+} (6 types)

(2) Draw the calibration line

←Click this icon and the calibration line is displayed on the right side of the chromatogram.

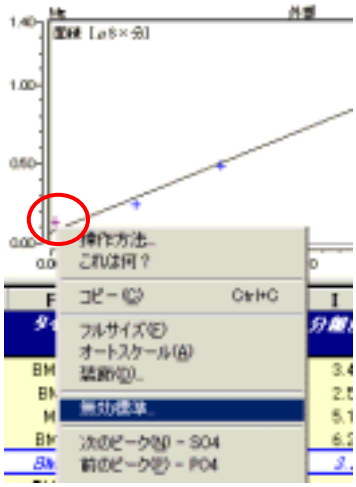


The calibration line is displayed on the right for the ion selected on the left screen.



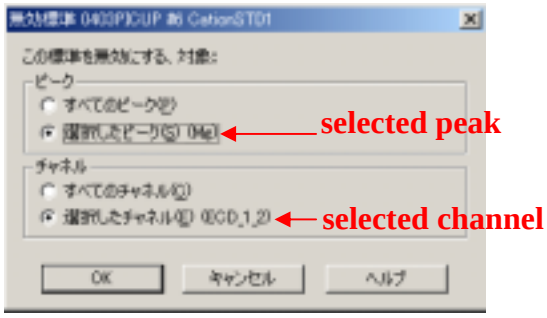
Thus the data not on the line is "invalid".

Right-click the applicable point and select Invalid standard.



Check Selected peak and Selected channel and click OK.

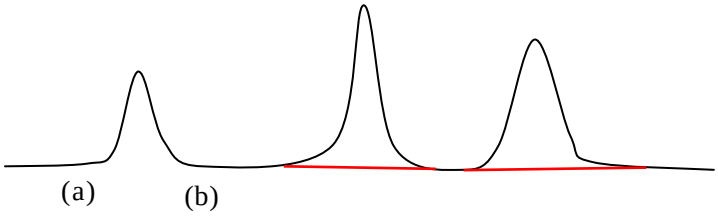
If oppositely you want to make invalid data valid, right-click the applicable point in the same manner and select Valid standard.



Peak adjustment

Peak detection is set to be executed automatically. If it is not detected properly, you should perform manual operation.

(1) Manual peak detection (when existing peak is not detected)



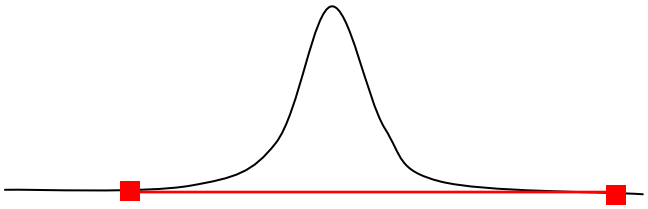
1. Click the right button of the mouse.
2. Select Tools then Peak insertion tool
3. Drag the cursor from the beginning of the peak (a) to the end (b) with the button pressed.

This draws the baseline (red), and it is recognized as the peak.

]

Peak insertion icon 

(2) Peak starting point and ending point adjustment



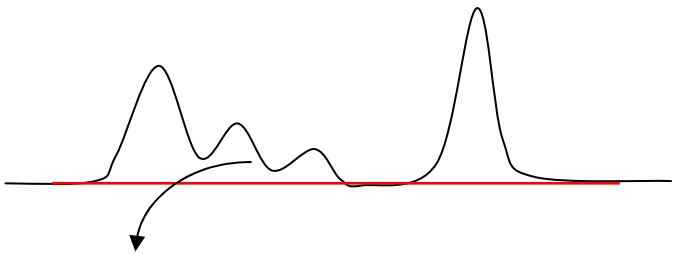
1. Click the right button of the mouse.
2. Select Tools and the Border tool.
3. Select the starting or ending point (■) you want to move and drag it to the desired position with the mouse.

This enables you to adjust the reading (starting point) and tailing (end point).

Border tool icon 

(3) Peak division

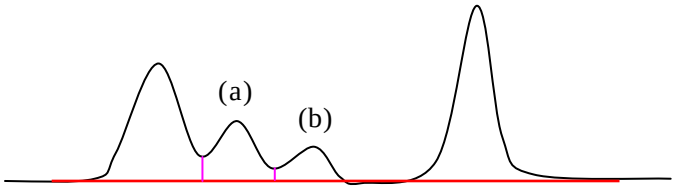
There are various ways to divide a peak. Here is a simple method:



1. Place the cursor on the peak to be divided and click the right button.

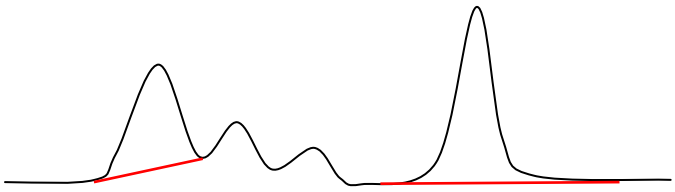
2. Select Change to main peak.

The peak then becomes as shown in the following figure.



3. Place the cursor on peak (a) and click the right button.
4. Select Delete peak.
5. Repeat the procedure for peak (b).

The main peak only is then detected.



Results print-out

-Data for each sample: Integral_anion / Integral_cation

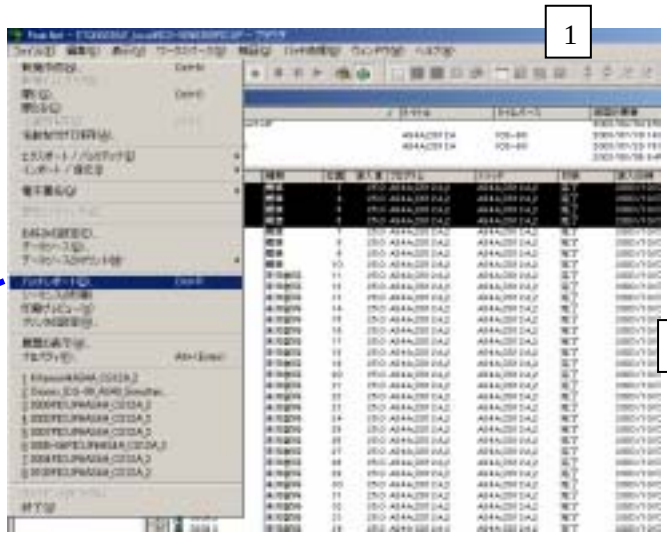
-Numerical value list: Summary input: With level cation

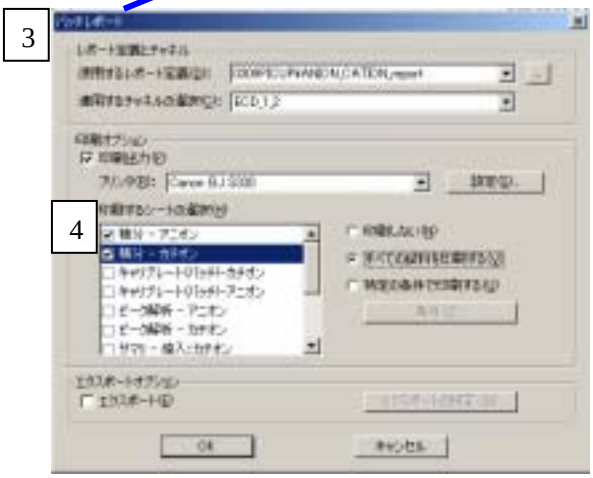
-Summary input: With level cation

-To summarize and output various types of analysis/sample data,

1.open the sequence of the data to be output (browser screen).

2. Select sample to be output.





3. File – Batch process report

4. Select sheet to be printed

-Under ordinary circumstances, select Integral_anion or Integral_cation

-Place a check in the box next to Print all samples for each sheet. (For standard sample, either Integral_anion or Integral_cation will do, so they may be output separately.)

5. OK

(For details, see the attached manual.)

Stopping the equipment

1. Turn the auto-suppressor power off.
   Wait 10 – 20 seconds.
   You only have to wait until air bubbles no longer come from the waste liquid.
2. Pump stop
   Click the Pump stop button on the control panel.
3. Gas pressure release
   To release the pressure remaining in the eluent bottle, just remove the tube.
4. Close Peak Net.
5. Turn the PC’s power off.
6. Turn the power tap off.
7. Close the nitrogen valve.