DETERMINATION OF NANO-MOLAR CONCENTRATION PHOSPHATE IN SEAWATER USING A LONG-PATH LENGTH WAVEGUIDE CAPILLARY CELL (LWCC)

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  - a long-path length waveguide capillary cell (LWCC)
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- Applications to field study
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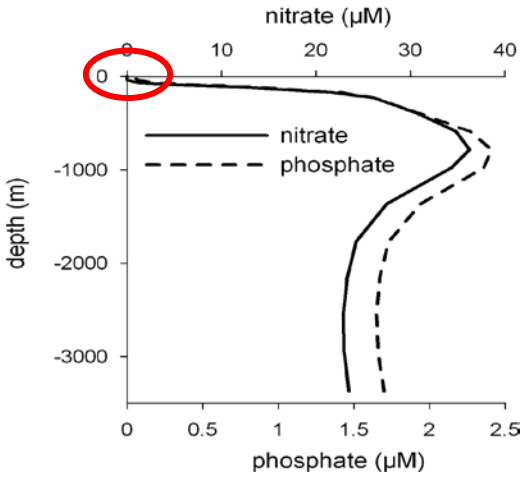
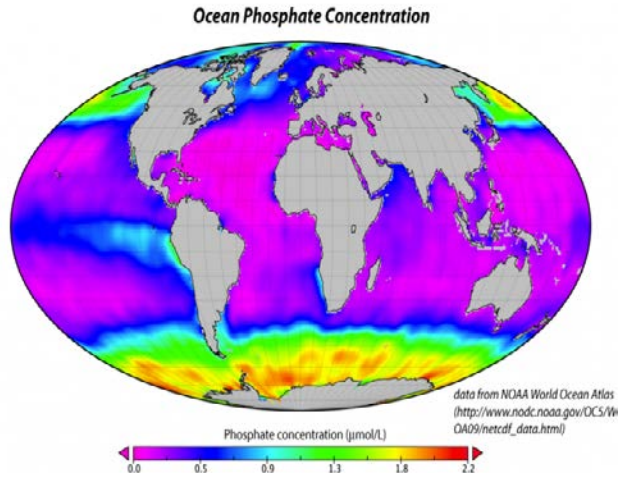
INTRODUCTION

Phosphate

- Importance of phosphate
  - **Essential Nutrient** for phytoplankton
  - Limiting Factor in primary productivity
- Deplete phosphate in surface water





40% of world oceans - oligotrophic

Principle of phosphate analysis

- **Murphy and Riley's molybdenum blue(MB)**

$$PO_4^{3-} + 12MoO_4^{2-} + 27H^+ \xrightarrow{Sb} H_3PO_4(MoO_3)_{12} + 12H_2O$$

Molybdate — phosphomolybdate complex

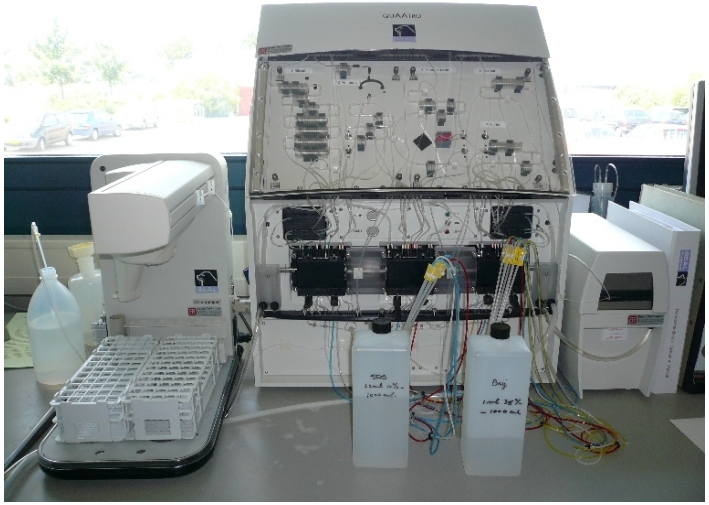
$$H_3PO_4(MoO_3)_{12} + C_6H_8O_6 \rightarrow \text{Phosphomolybdenum blue complex}$$

Ascorbic acid

  - Antimony Potassium Tartrate (Sb) = catalyst
  - Sodium dodecyl sulfate(SDS) = surfactant
  - 660 – 880 nm
  - Interference : Arsenate, **Silicate**

Conventional instrument

- Auto analyzer(SCFA,FIA)
  - 1 - 5 cm cell , 880 nm
  - Detection limit : 0.3 µM (300 nM)
  - Difficult to apply underway system



- **Need an analysis system for nano-molar level phosphate and for continuous measuring system.**

Nano-molar phosphate analysis

- By application of LWCC
  - Optical path length of the measurement cell

$$\uparrow E = -\log I/I_0 = \varepsilon * C * L \uparrow$$

E : Absorbance ε Molar extinction C : Concentration **L : Path Length**

Generally 0 – 2

$$\downarrow C = \frac{E}{\varepsilon L \uparrow}$$

constant

  - Previous Studies
    - Lei et al., 1983 –1m cell
    - Zhang et al., 2002 – 2m cell
    - Li et al., 2008 – 2m cell
  - **These studies applied for discrete sample, not continuous analysis.**

The aim of this study

- To set up **a nano-molar phosphate analysis system with a 1m-long-pathlength waveguide capillary cell(LWCC)**

- To apply to field study (in-situ continuous measurement)

INSTRUMENT SETUP

Selection of Wavelength for LWCC

- Spectrum of phosphomolybdenum blue

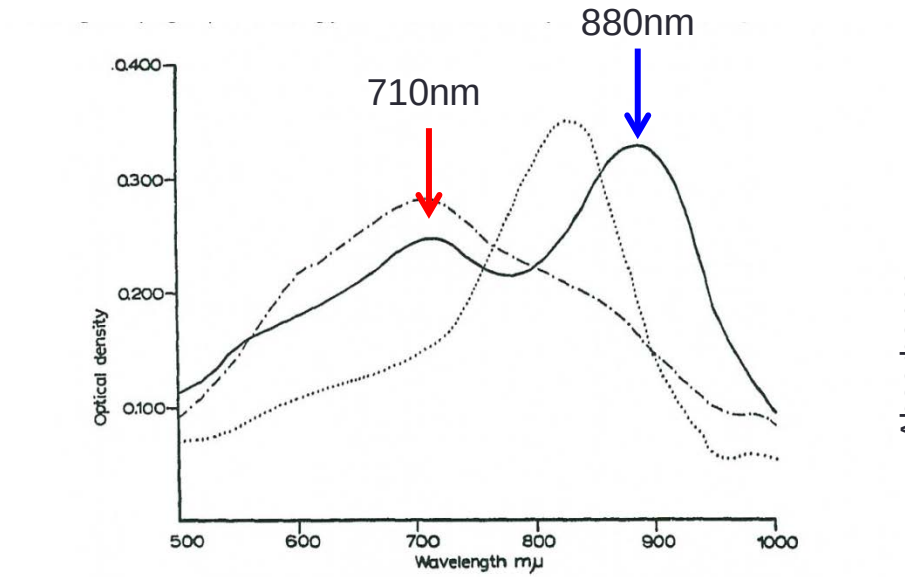
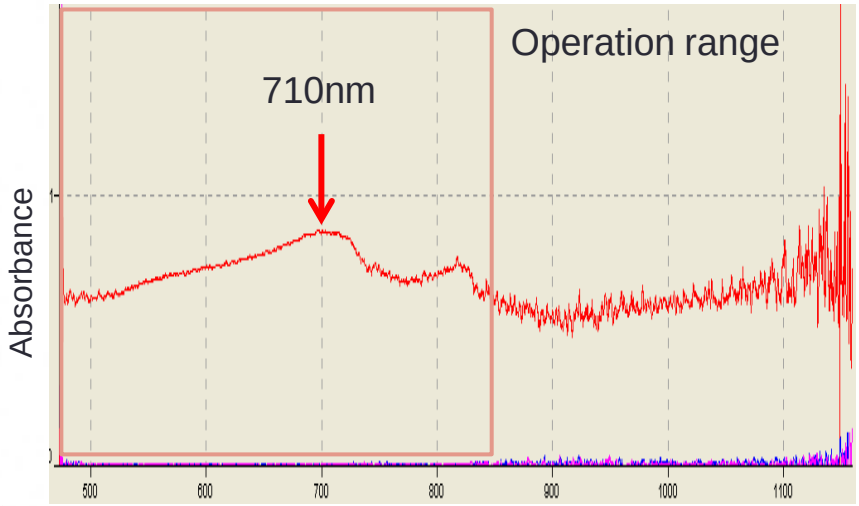


Fig. 1. Absorption curves for molybdenum blue formed with various reducing agents (3.0 μg P as PO_4^{3-} in 50-ml flasks; 7.62-cm cells) ·—·—·— reduced with stannous chloride; . . . . . reduced with ascorbic acid; ——— reduced with ascorbic acid + antimony.

※ Murphy and riley (1962)

- LWCC



Optimization of analytical procedures

1. Interferences
2. pH
3. Proton and molybdenum ratio
4. Temperature

Interferences

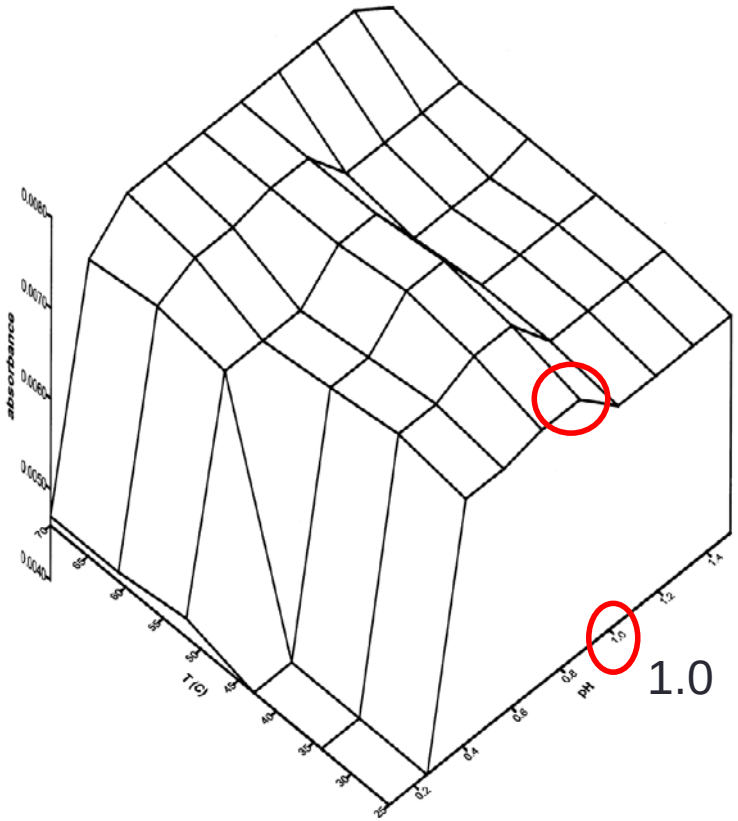
- Arsenate
  - Low concentration in seawater (~20 nM)
  - Long reaction time with molybdate (90 mins)
- Silicate
  - Phosphate Concentration interfered from 2 μM of silicate

	70 ℃	95 ℃	**Room Temp.**
P (nM) interfered from 2μM SI	0.8	60.6	$< 8 \times 10^{-5}$

  - Long reaction time (10 mins)
- **Solutions**
  - Short reaction time (3 mins)
  - Room temperature (27 ℃)
  - Short interval of time between the reagent injections

Chemical conditions

- pH = 1.0



Absorbances of 1uM phosphate as a function of temperature and final solution pH

※ Zhang. Talanta (1999)

- $[H^+]/[Mo] \approx 70$

Time for maxium absorbance

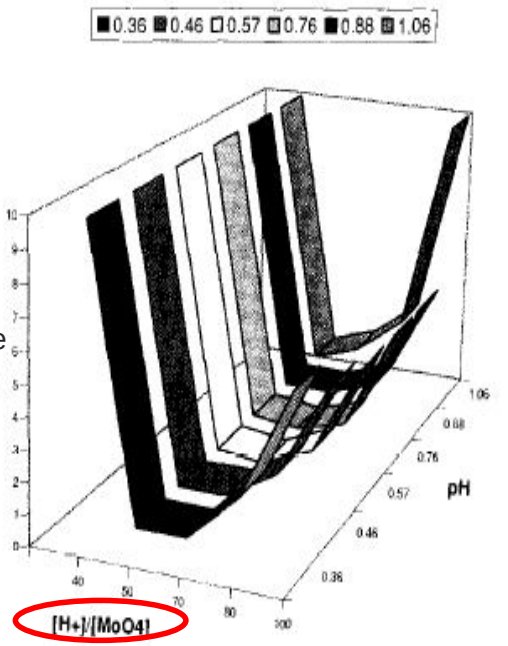


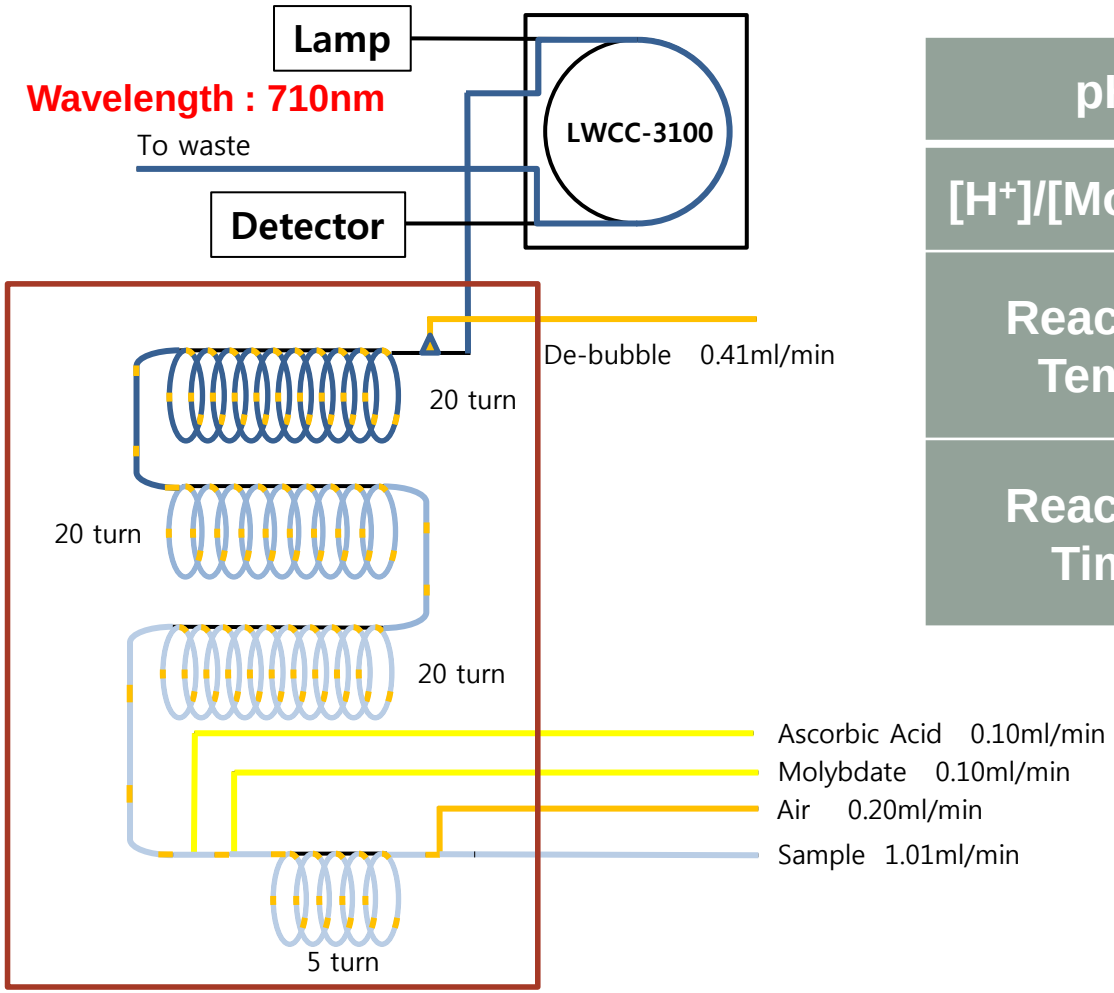
Fig. 5. Time required for development of maximum absorbance. 100 μg P/l. Bar represents key to pH values.

50< ratio <80 : Short reaction time

※ L. Drummond, W. Maher. Analytical Chemica Acta (1995)

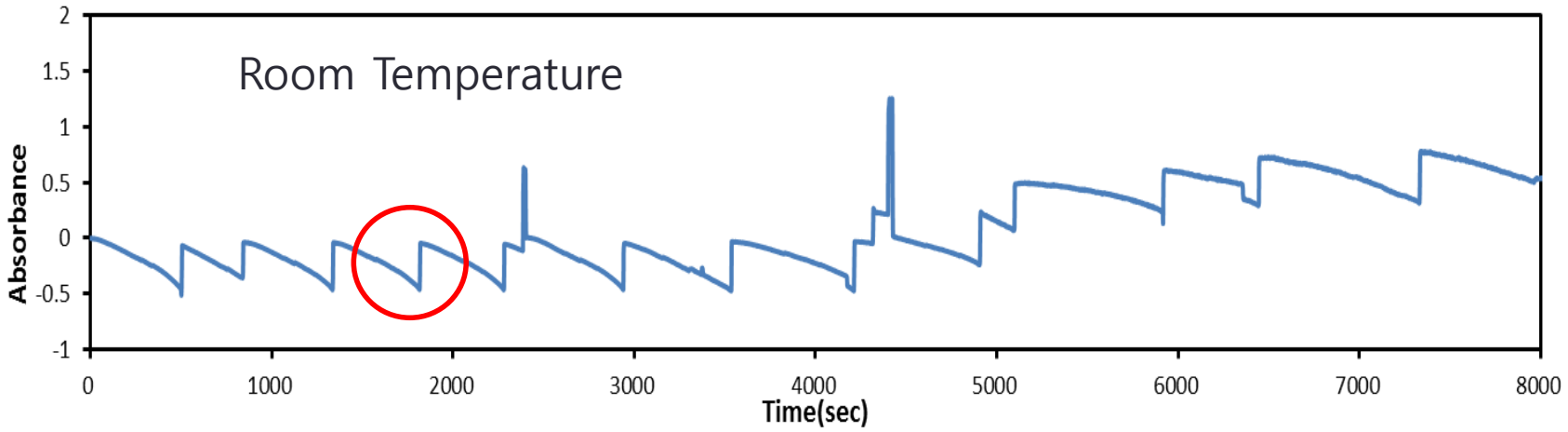
Configuration of system

- Flow system Combined with LWCC



pH	0.86 ~ 0.89
$[H^+]/[Mo]$ ratio	≈ 70
Reaction Temp.	27℃
Reaction Time	3 min

Bubbles in the Cell

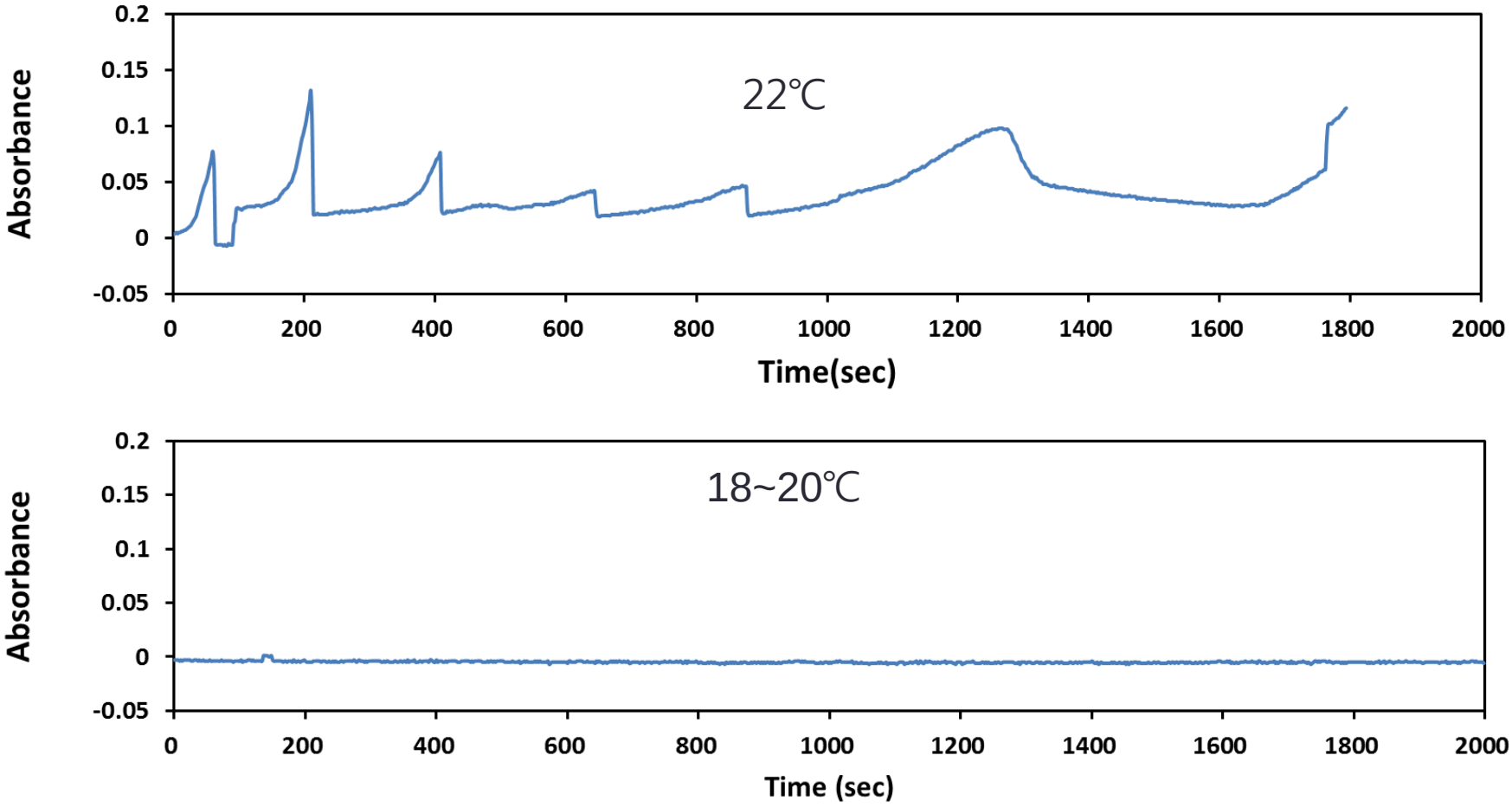


- Problem – Micro-bubbles

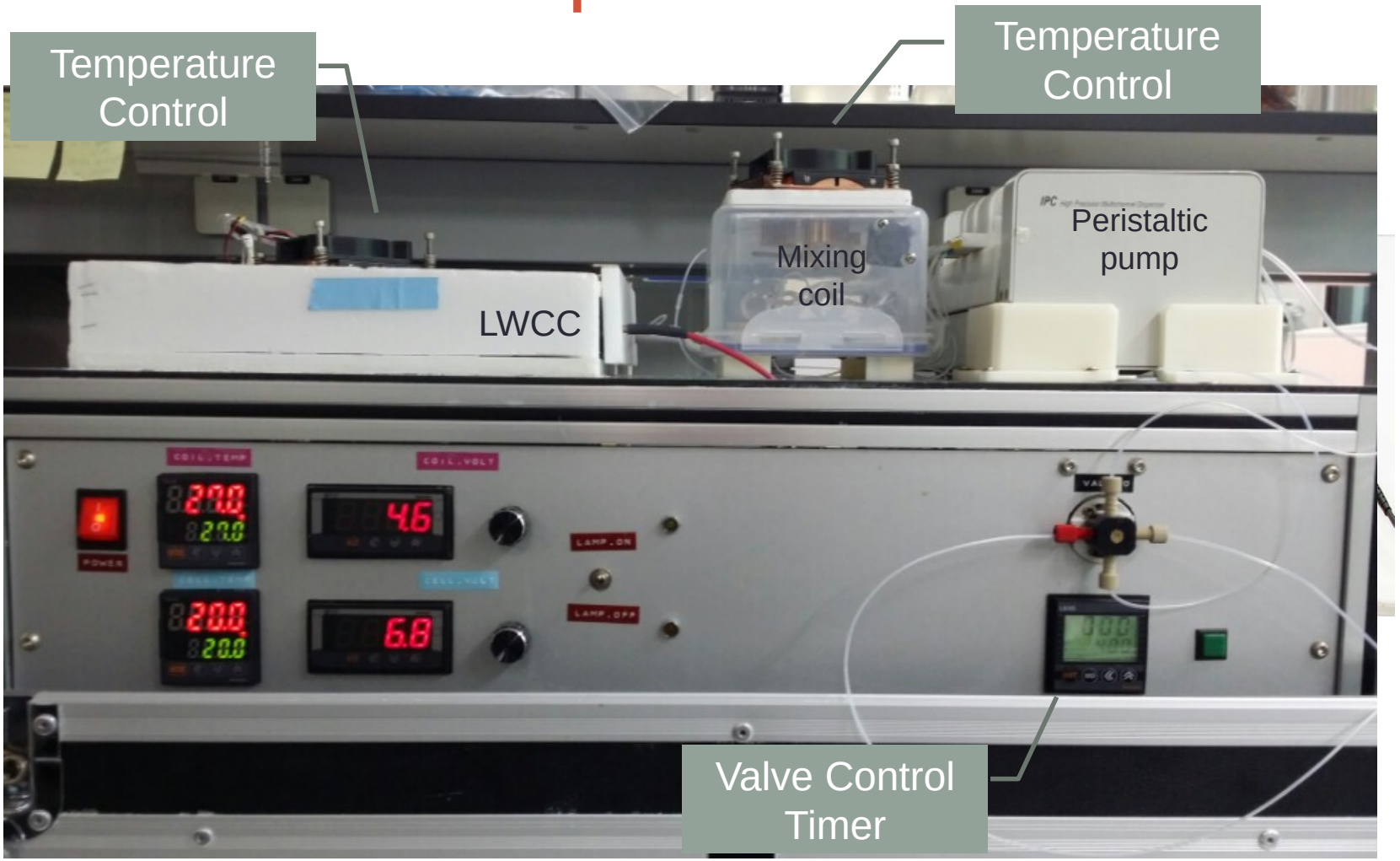
1. degassing of sample → Difficult to apply continuous system
2. Inline degasser → Make the system Bulky
3. Increase Gas Solubility : Low Temperature

Temperature

- Temperature control – 18~20℃



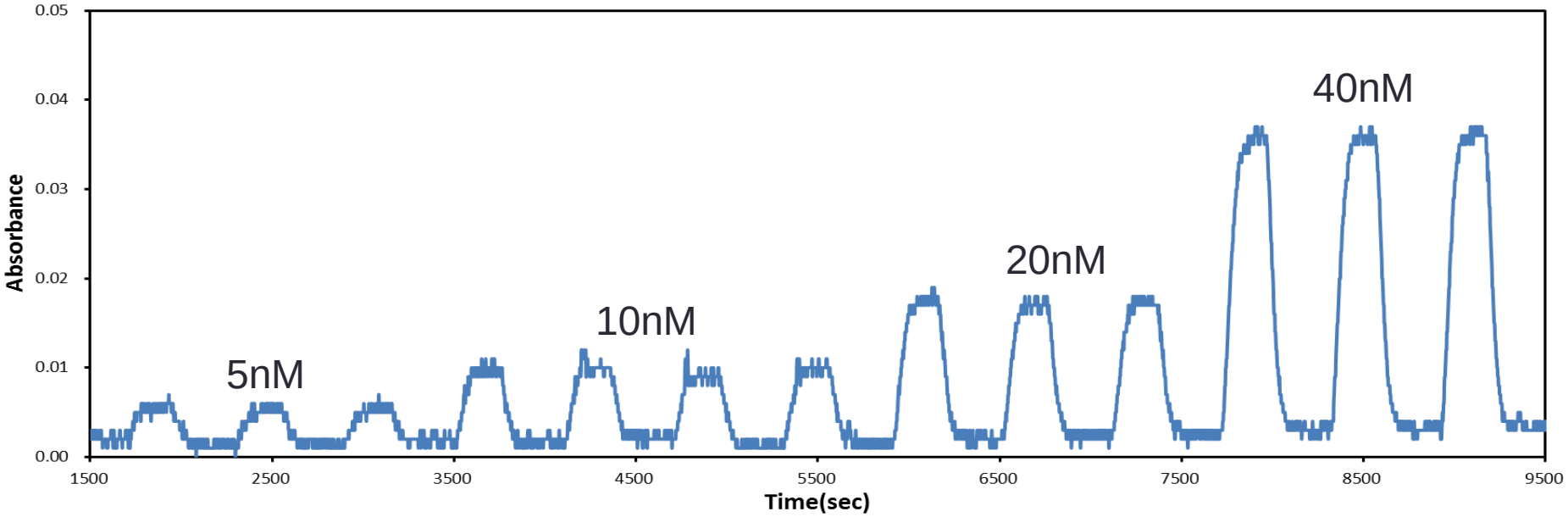
Instrument setup



Validations

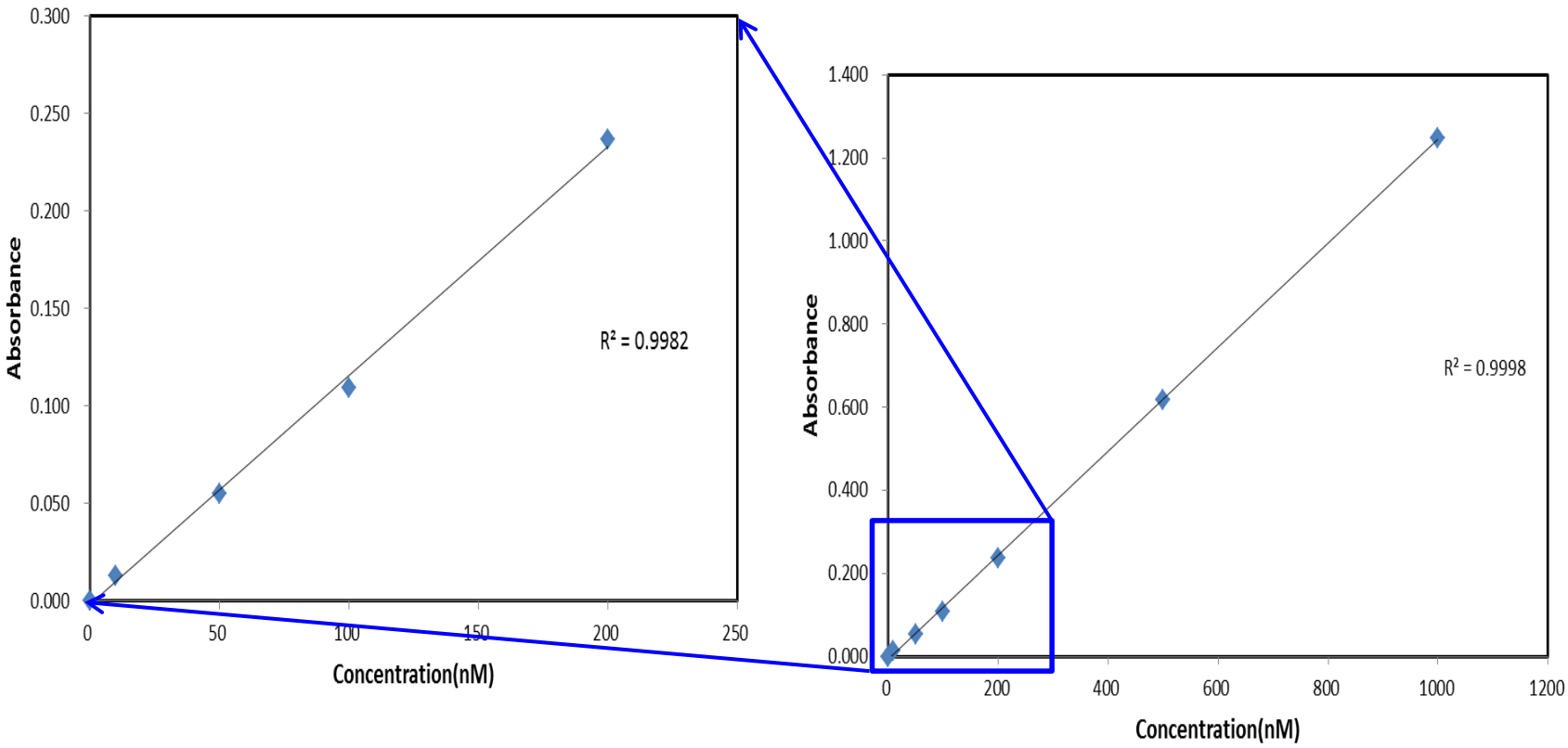
1. Linearity
2. Reproducibility
3. Repeatability

Standard peaks

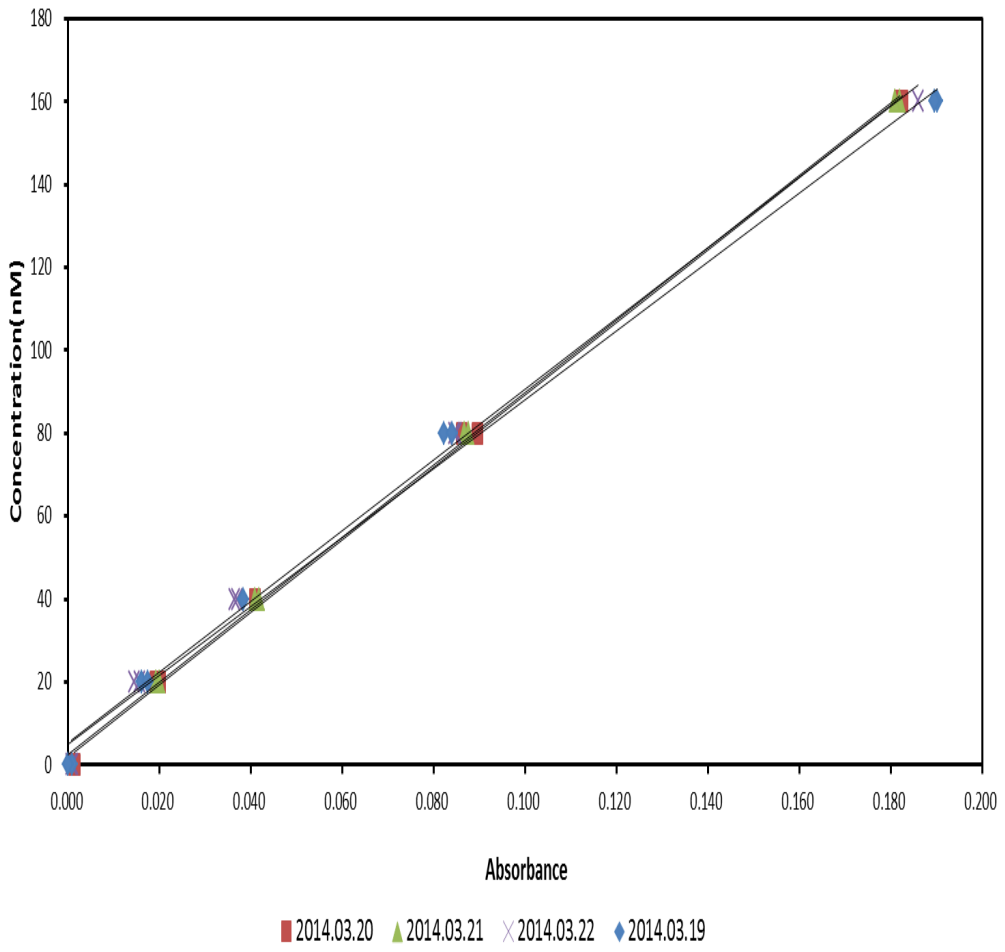


- Standard : K_2PO_4
- Working standard is diluted by artificial seawater
- Base : Artificial Seawater
- Sample/wash times : 4min : 4min

Linearity


0.300
0.250
0.200
0.150
0.100
0.050
0.000
Absorbance
R² = 0.9982
0
50
100
150
200
250
Concentration(nM)
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
Absorbance
R² = 0.9998
0
200
400
600
800
1000
1200
Concentration(nM)

Reproducibility



$y = 831.45x + 5.0848$
$R^2 = 0.9951$

$y = 853.11x + 5.2491$
$R^2 = 0.9937$

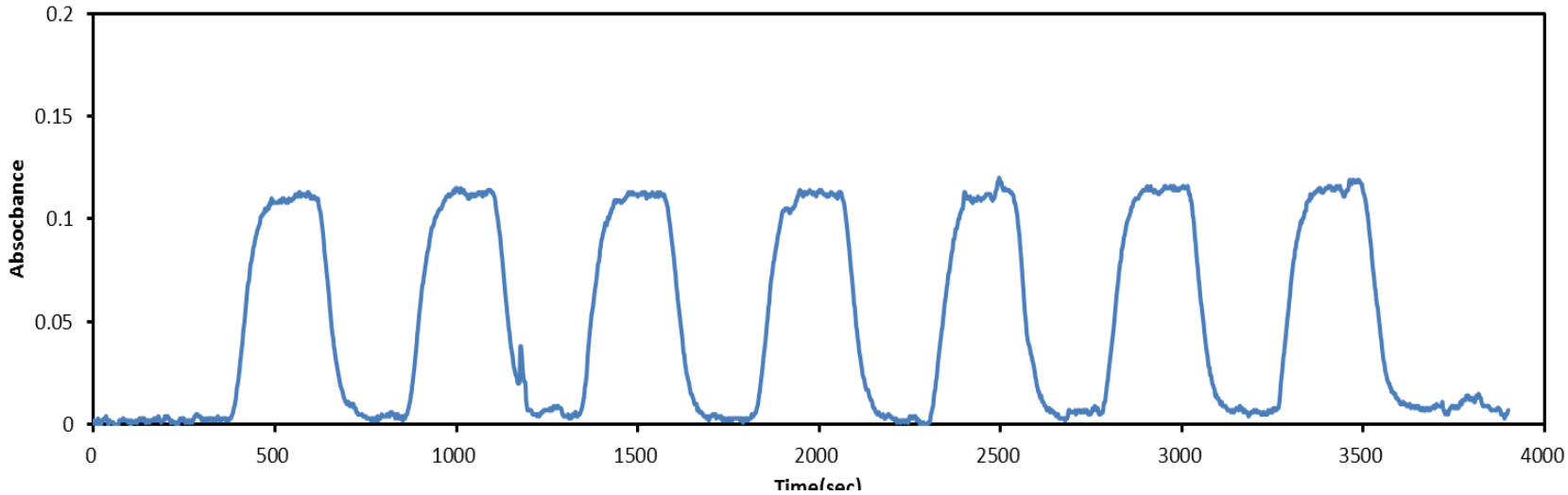
$y = 873.17x + 2.5482$
$R^2 = 0.9994$

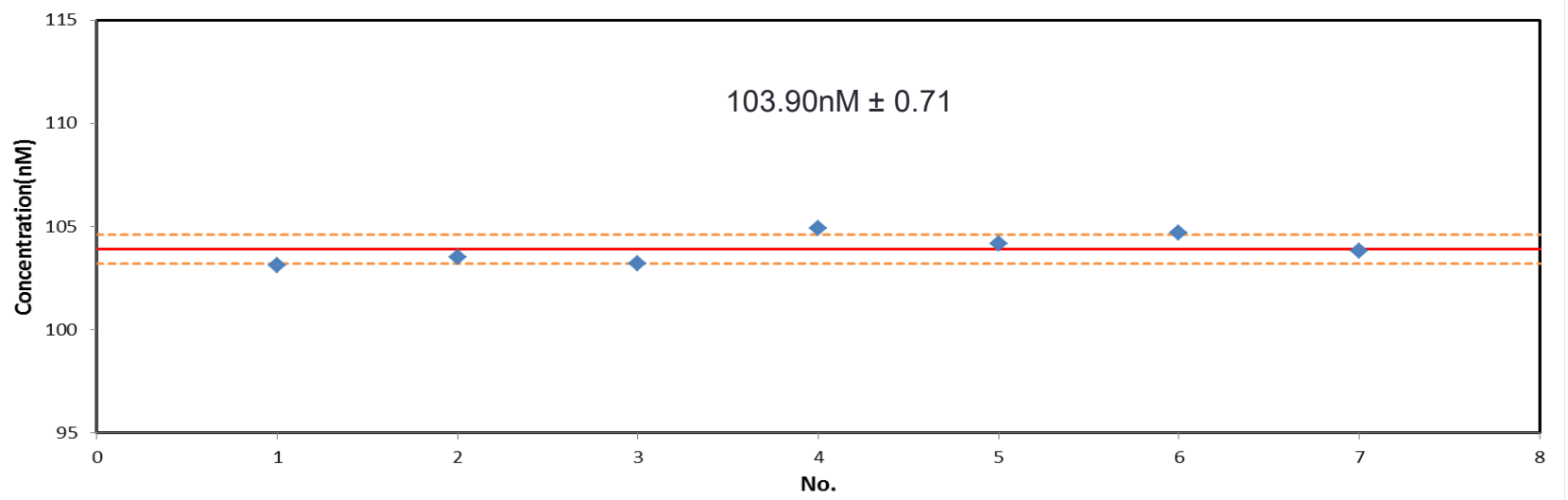
$y = 873.24x + 2.023$
$R^2 = 0.9986$

Average :

$y = (851.485 \pm 25.306)x + (2.971 \pm 1.720)$

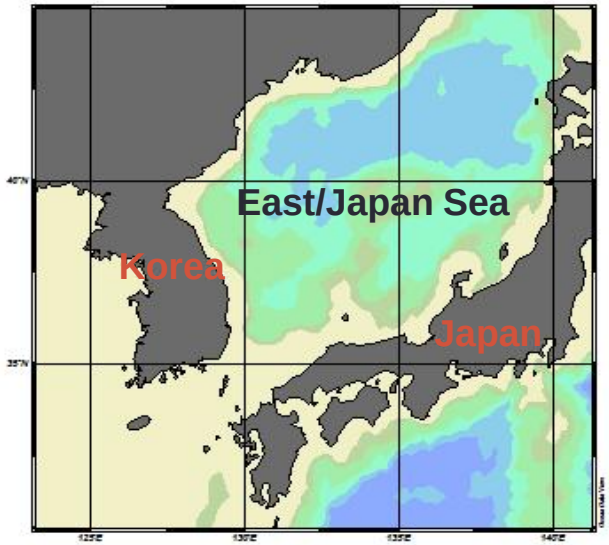
Repeatability



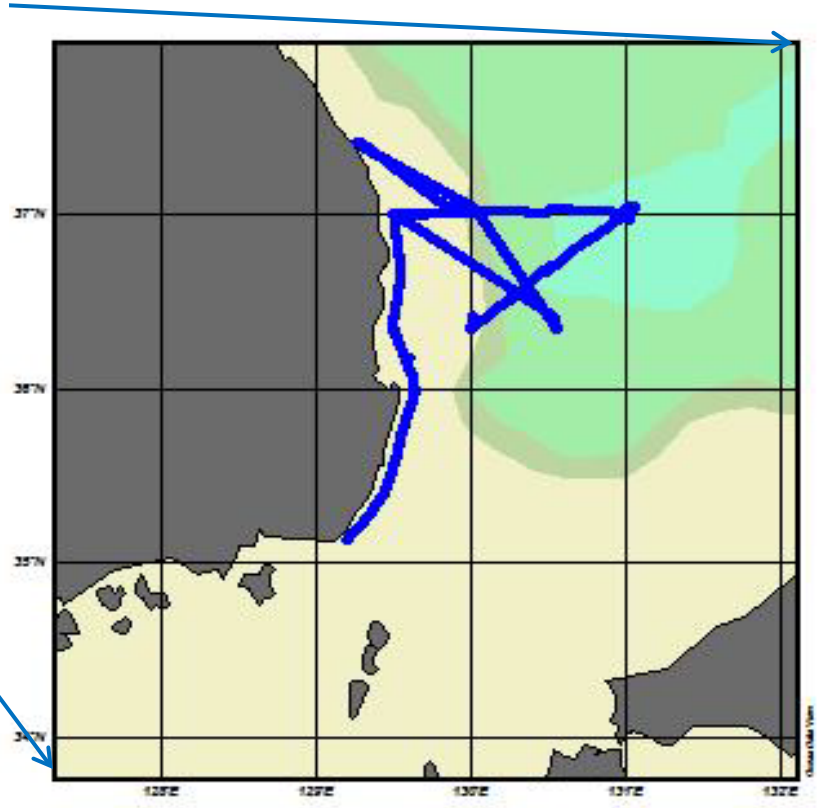


APPLICATIONS TO FIELD STUDY

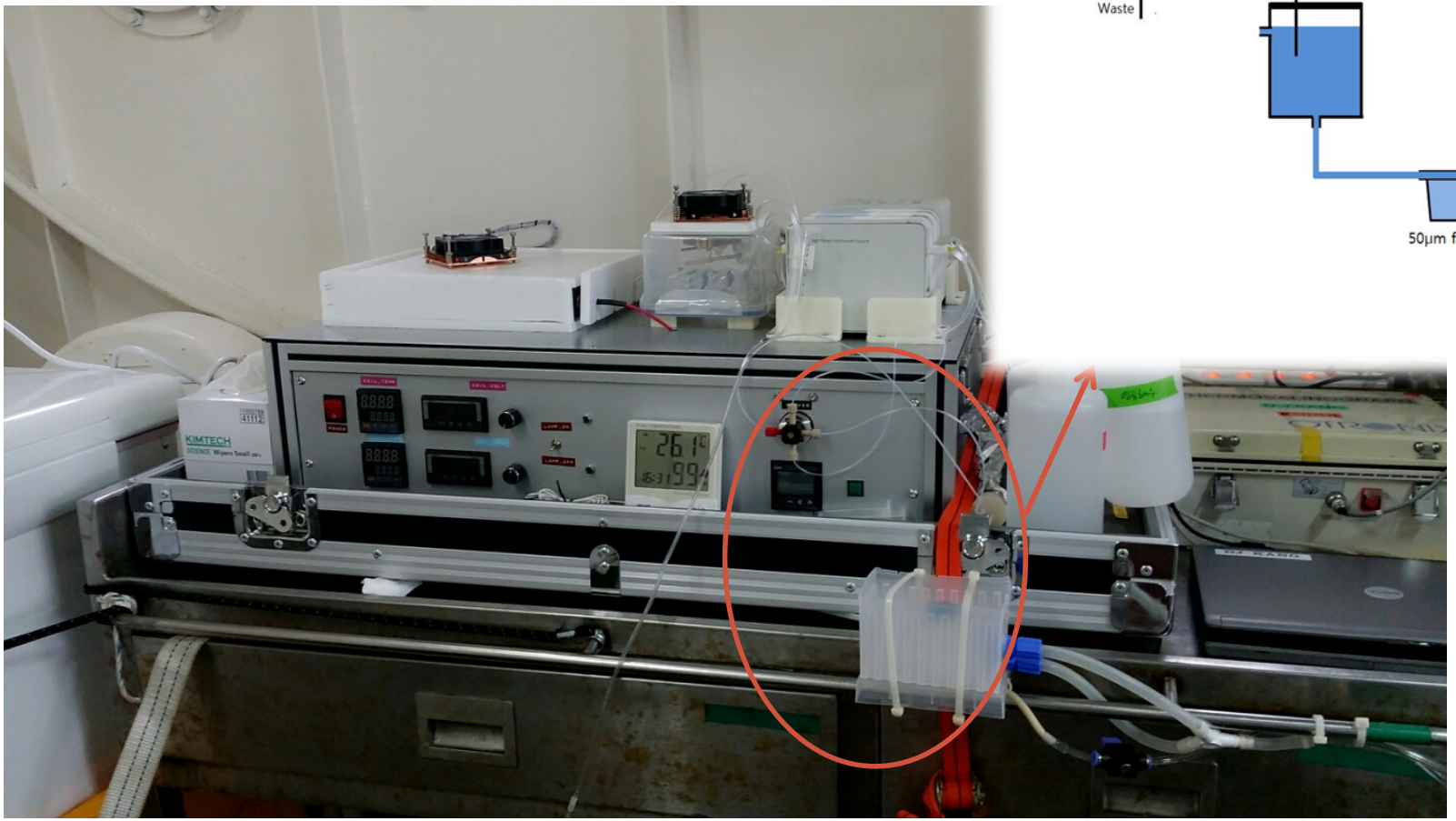
Cruise

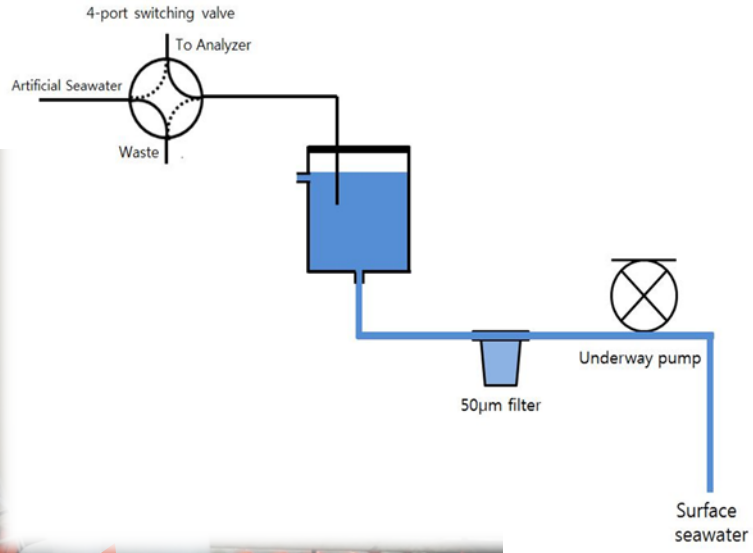


- **Date : Aug.19 – 24, 2014**
- **R/V Eardo(KIOST)**
- **Region : East/Japan sea**

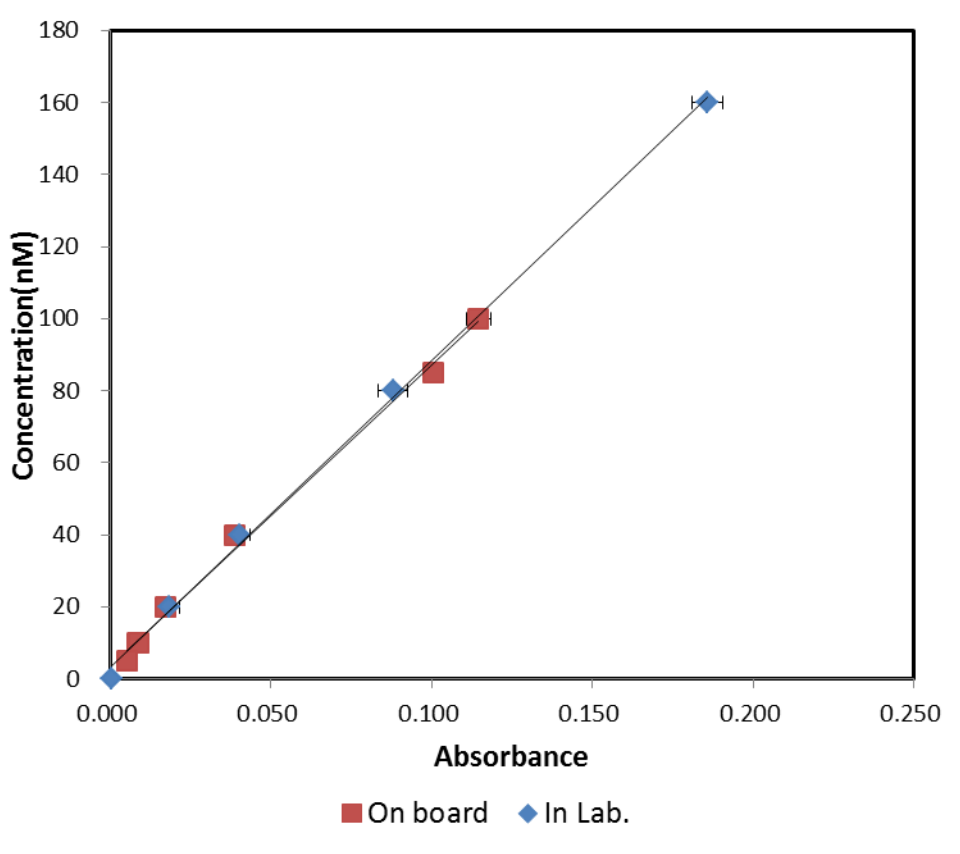


On Board Continuous Measurement





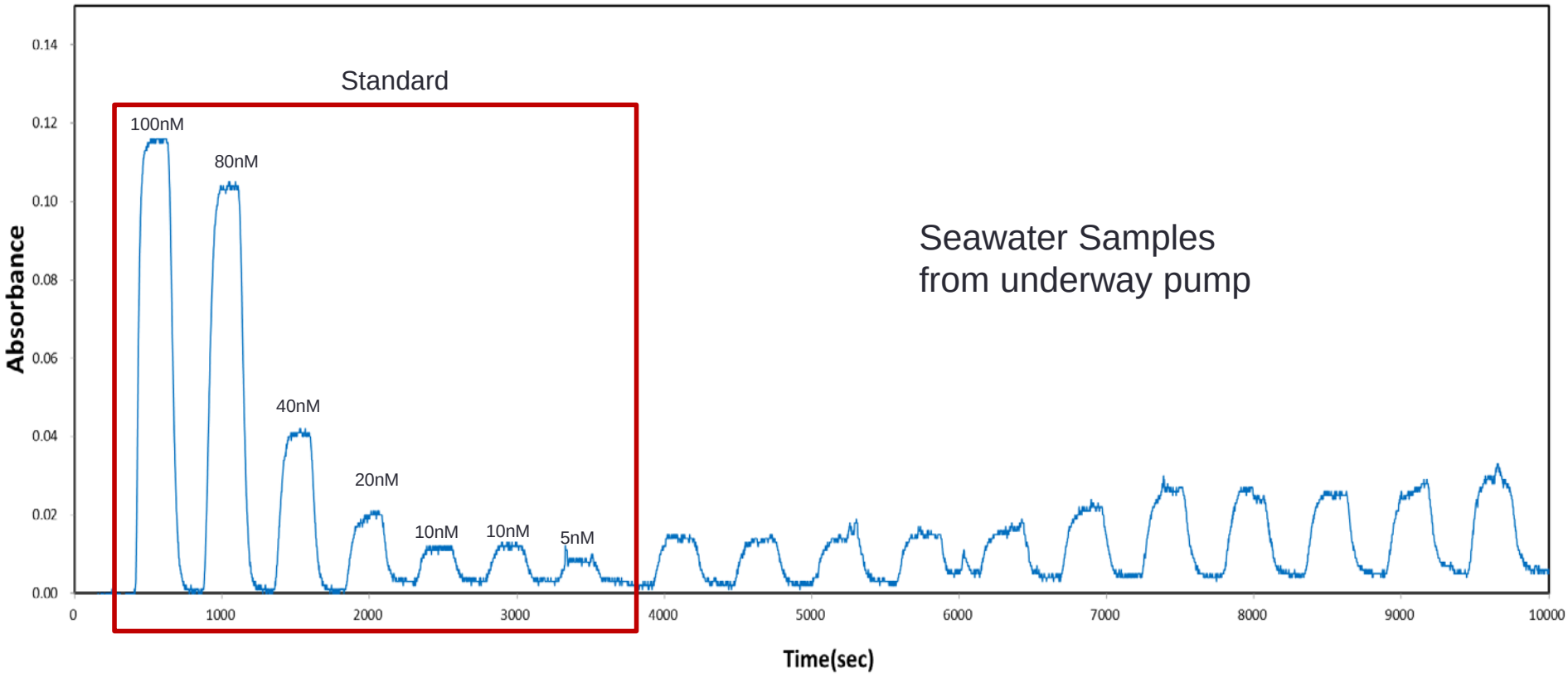
Calibration Curves



$y = (851.485 \pm 25.306)x + (2.971 \pm 1.720)$
$R^2 = 0.9984$

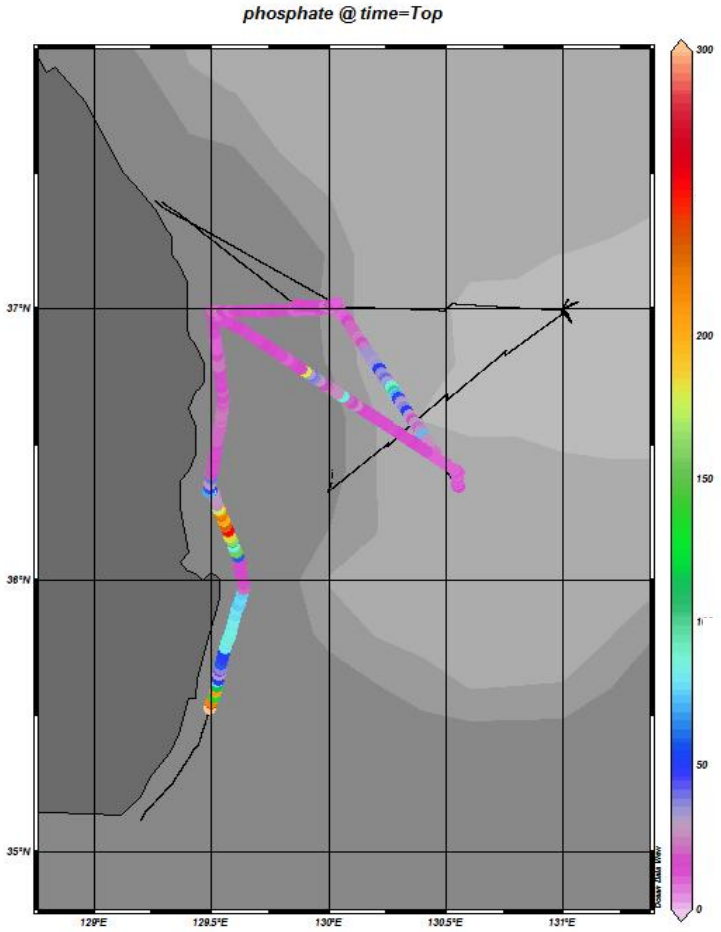
$y = (820.483 \pm 18.200)x + (5.033 \pm 1.300)$
$R^2 = 0.9958$

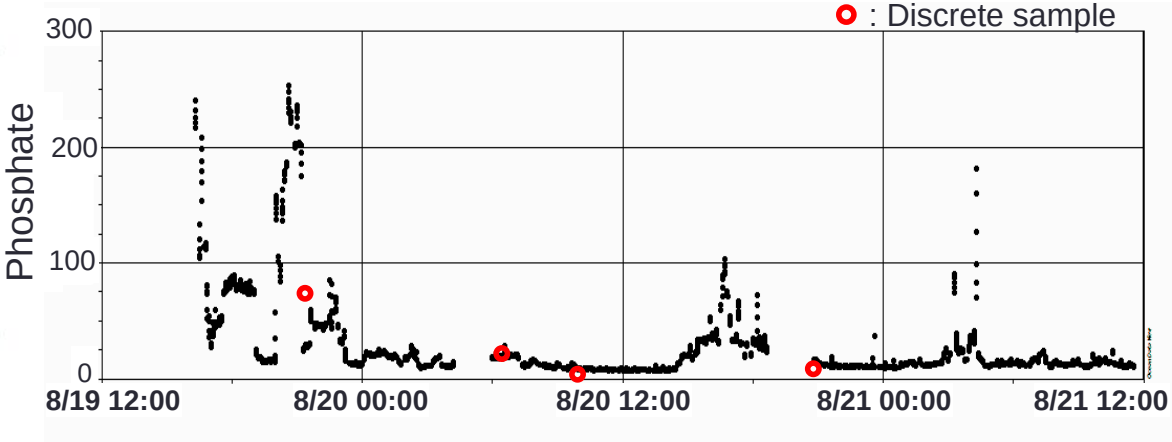
Peaks

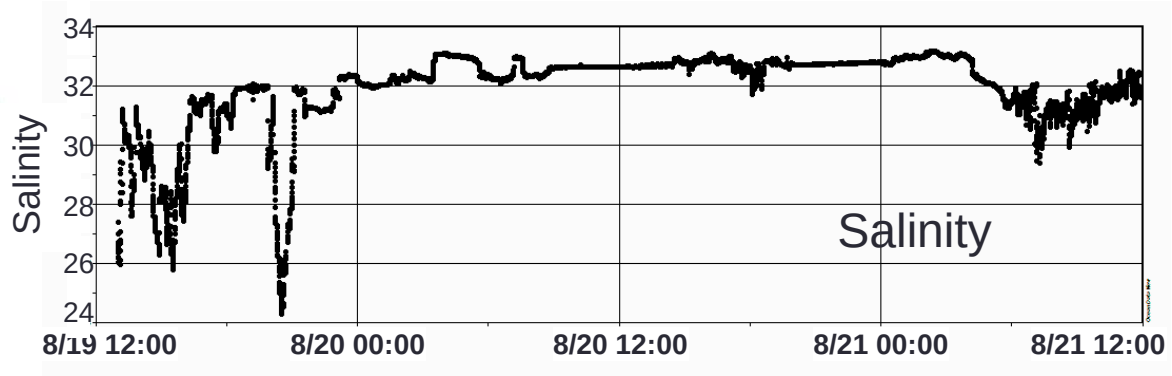


Sample : wash = 4min : 4min

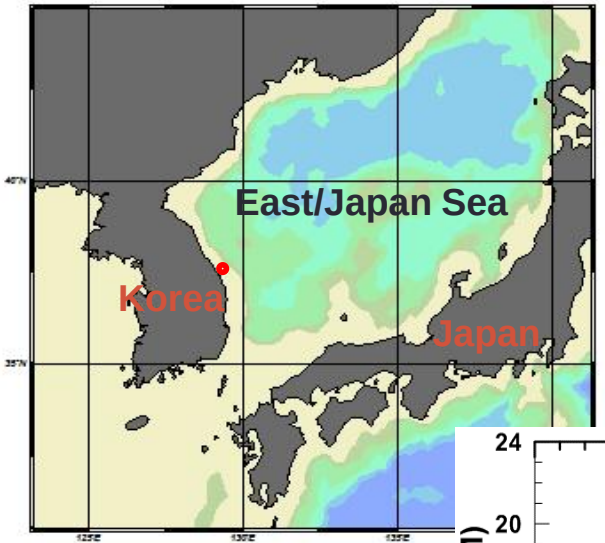
Continuous Spatial Measurement



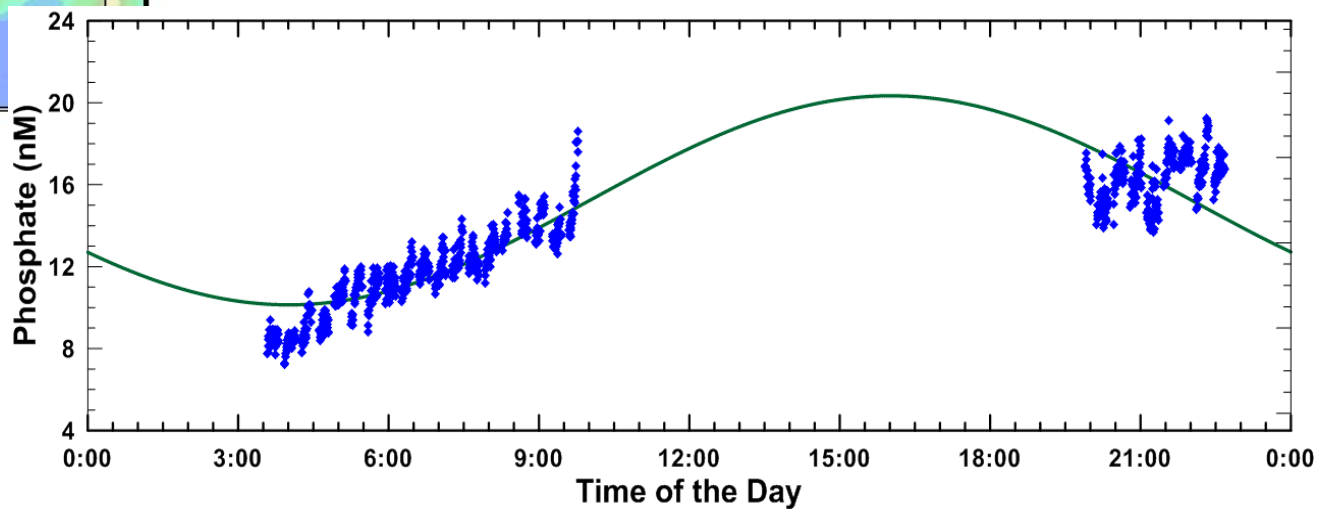




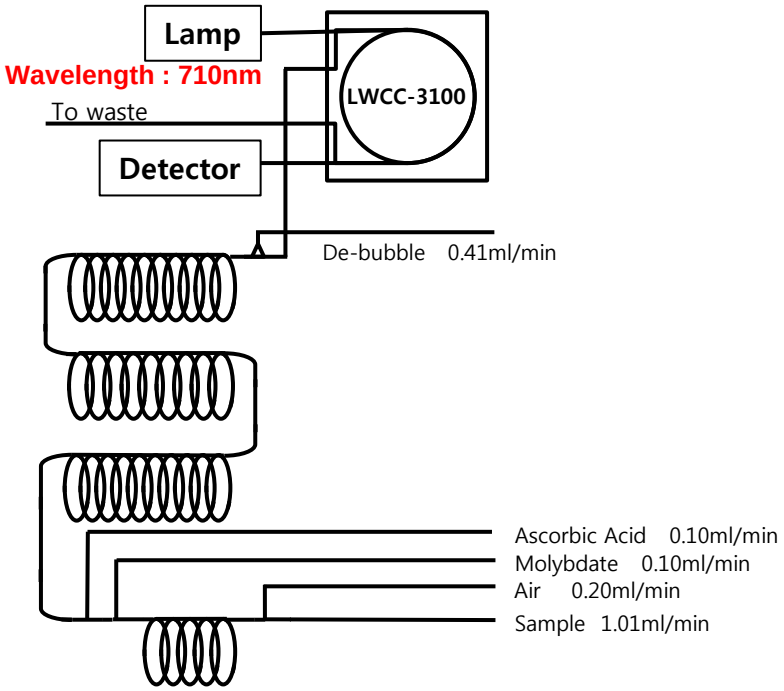
Continuous Time-Series Measurement



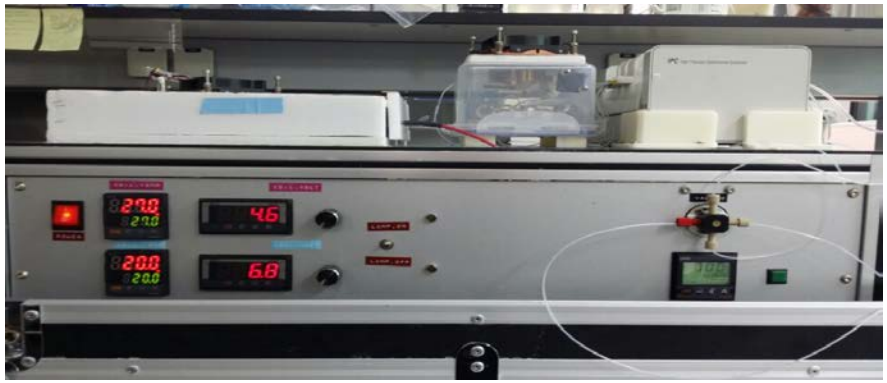
- **Date : Oct. 6-10**
- **R/V Tamsa(SNU)**
- **Region : East/Japan sea**



Summary



pH	0.86 ~ 0.89
$[H^+]/[Mo]$ ratio	≈ 70
Reaction Temp.	27℃
Cell Temp.	18 ~ 20 ℃
Reaction Time	3 min



- Nice to apply continuous spatial and time-series measurement of phosphate

THANK YOU