Metrological Test Technology of Marine Instruments in Ecology Monitoring

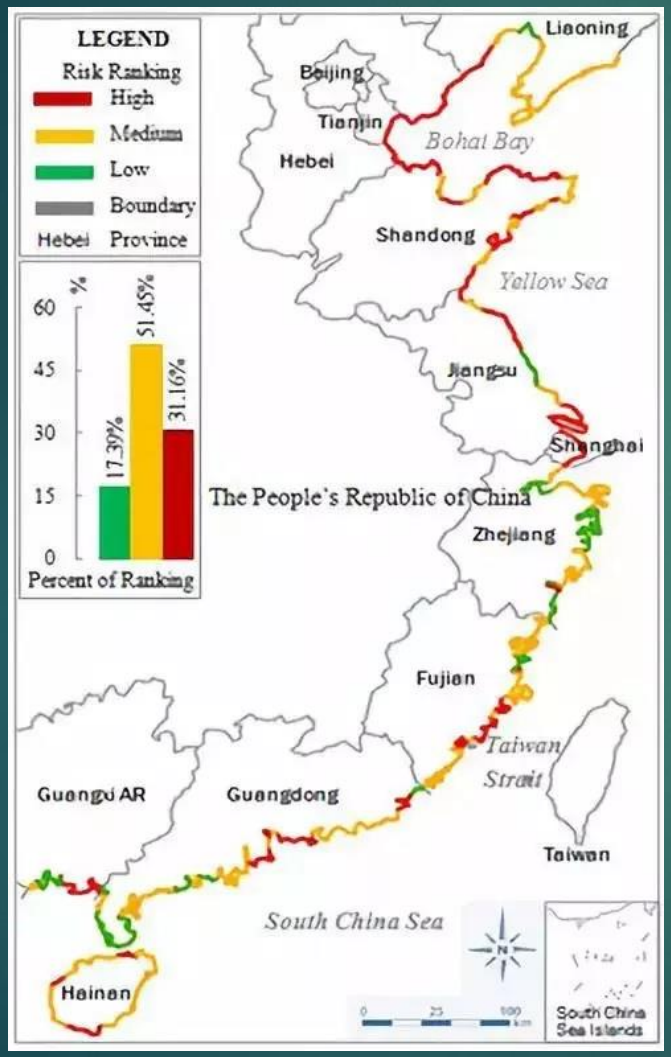
CHAOYING SHI

NATIONAL CENTER OF OCEAN STANDARDS AND METROLOGY

Contents

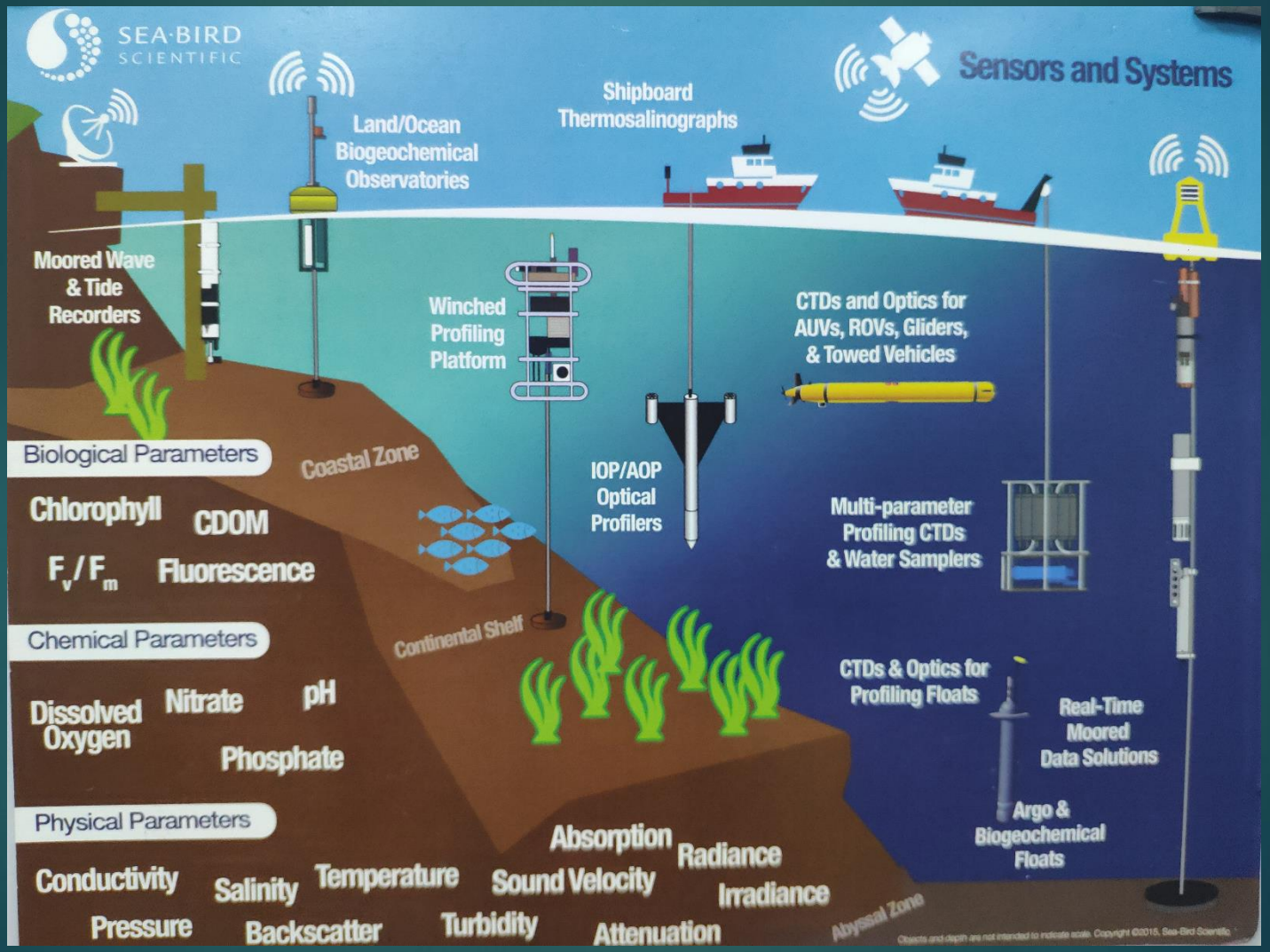
- 1. Introduction
- 2. Metrological Test Technology
- 3. Standard Materials
- 4. Research in future

1.Introduction



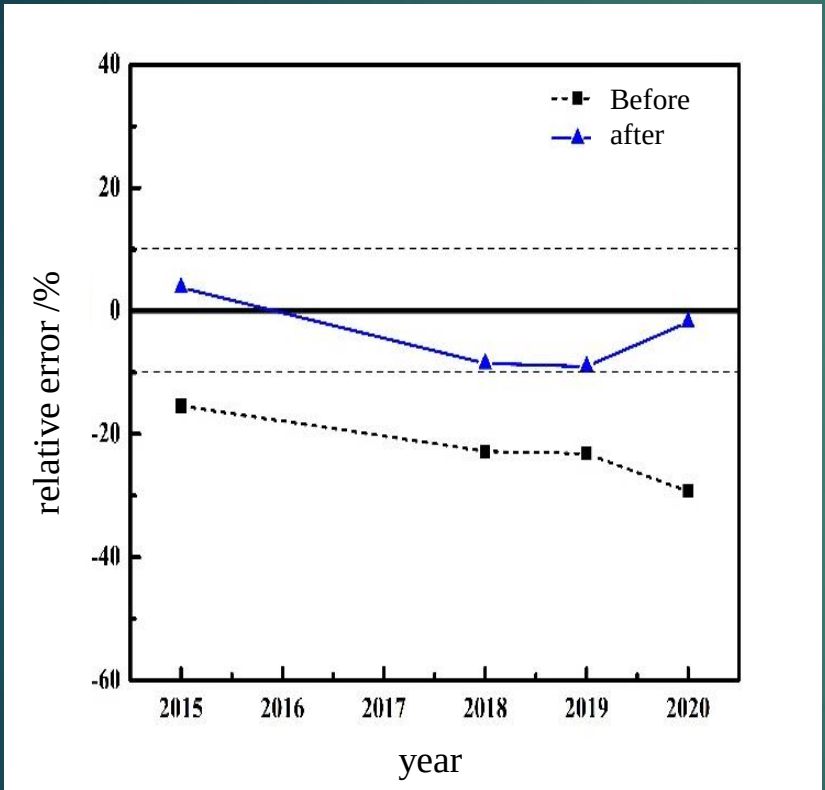
- Long coastline
- Rich in marine resources
- Wide range of ecological monitoring

Marine Instruments and Parameters in Ecology Monitoring



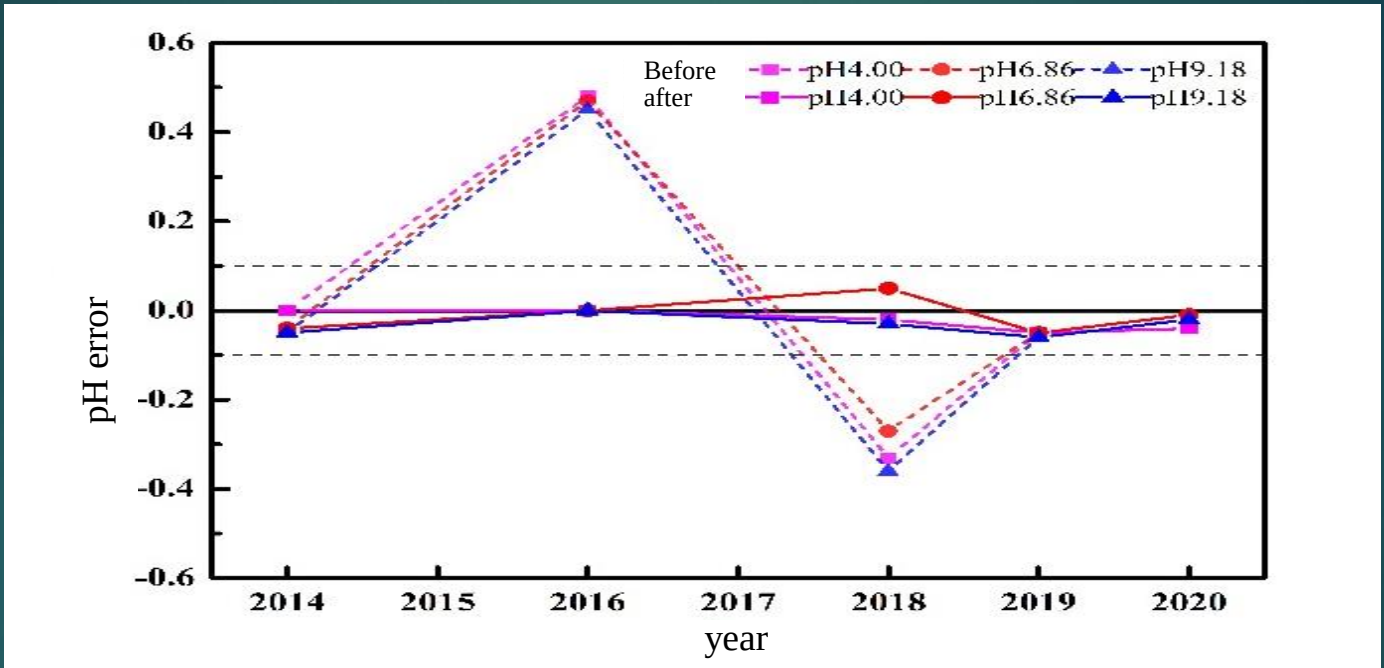
（From Seabird scientific）

Errors variations of turbidity sensors after calibration



- Calibration can effectively control the error of the sensors
- When the turbidity sensor is used at sea for a long time, its voltage value will drift with time which will cause large deviation

Errors variations of pH sensors after calibration



- After 2 years' long-term use on the sea, the pH error was far exceeded the maximum permissible error(MPE). Especially in 2016, the maximum error of initial indication reached 0.48.
- Properly planning the calibration frequency will help to improve the accuracy of the sensor.

It is important to calibrate the instrument in Ecology Monitoring

And

Regularly

2. Metrological Test Technology

Calibration and Testing services

- Test for DO sensors
- calibration for pH sensors
- calibration for turbidity sensors
- calibration for nutrient analyzers
  - Nitrate
  - Nitrite
  - Ammonium salt
  - Silicate
  - Phosphate

We have ever calibrated such instruments as follows

Turbidity Sensor

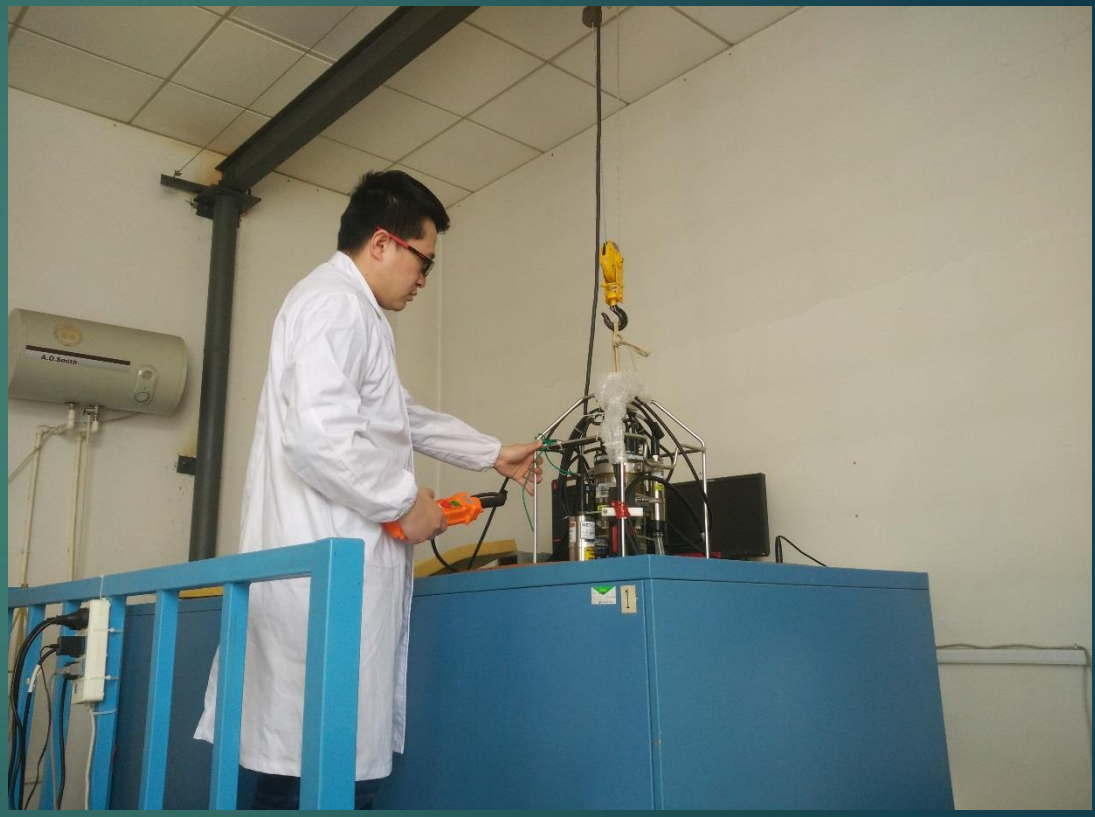
Nutrient Analyzer

DO Sensor

SBE27 pH sensor

2.1 Test of DO sensors

- **Thermostatic bath**: provide constant temperature environment
- **Seawater**: simulate marine environment
- **High purity gases**: change dissolved Oxygen in seawater
- **Winkler Titrations:** provide standard value of DO in seawater



Winkler Titrations

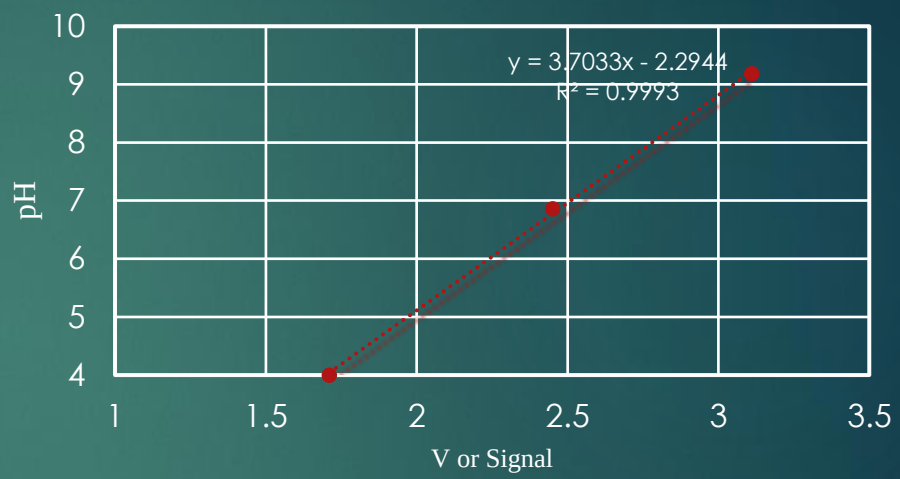
Quality titrator with automated endpoint detection.
Accurate dispenser

Quality, calibrated Reagent dispensers

Keep samples dark at constant temperature, not cooler than the draw temperature.

2.2 Calibration of pH Sensors

- **Thermostatic bath**: provide constant temperature environment
- **pH standard buffer**: provide standard value
- **thermometer:** Detect temperature

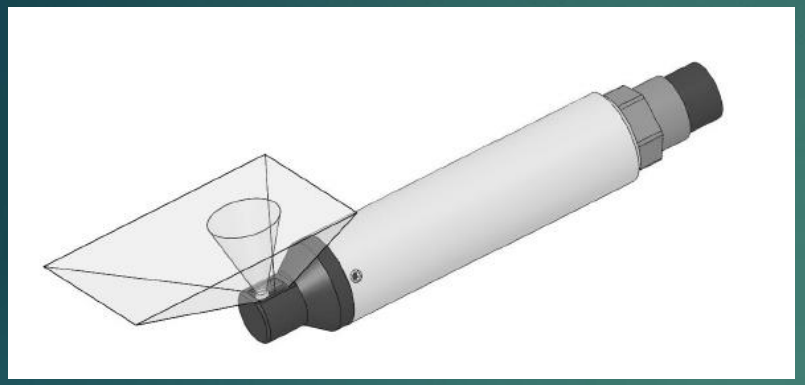


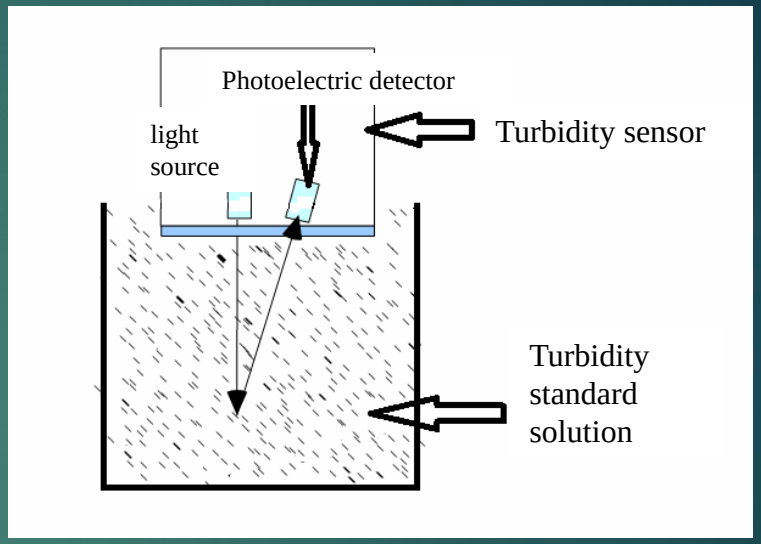
Provide Calibration factors

$pH=7+（Volt-Offset）/（1.98416*10^{-4}*T*slope）$

2.3 Calibration of Turbidity Sensors

Boundary effect





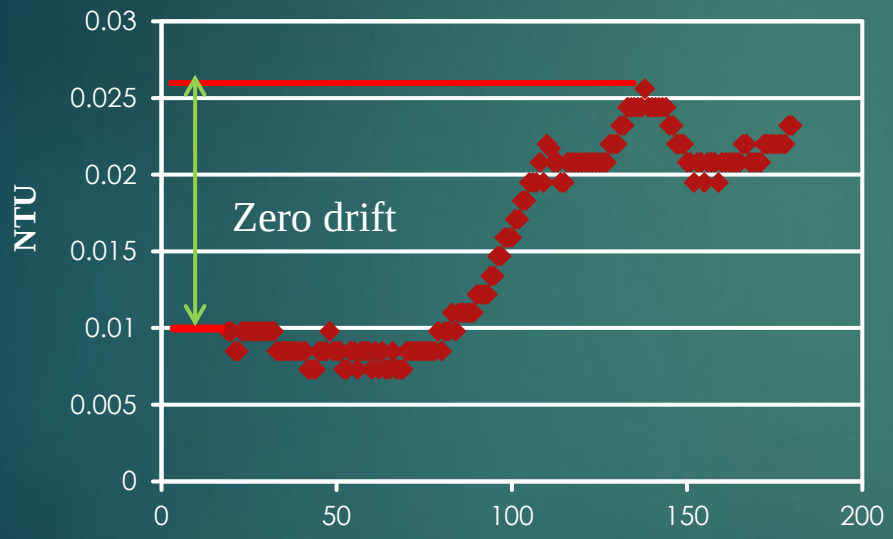
Lateral luminescence

Vertical luminescence

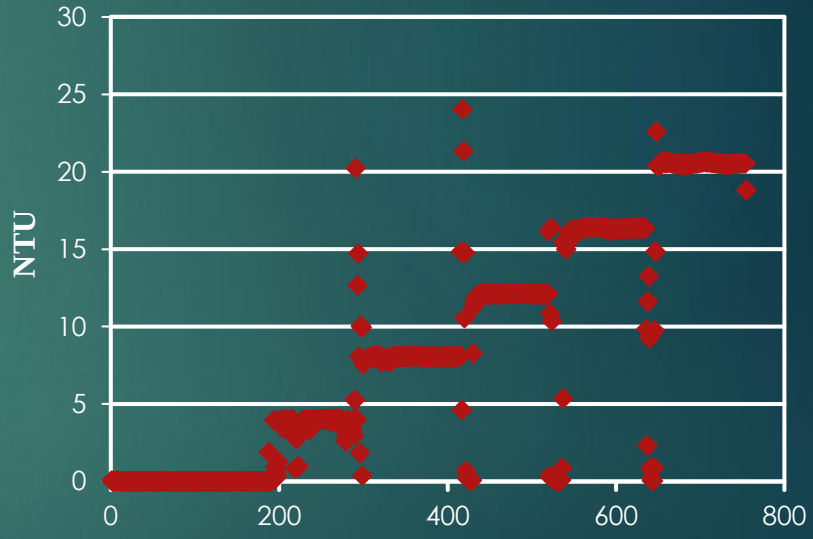
- The containers in the laboratory will have a boundary effect on optical sensors such as turbidity.
- It is necessary to control the size of the container, which can overcome the boundary effect without wasting the standard solution.

2.3 Calibration of Turbidity Sensors

Zero drift: the maximum amplitude to the range

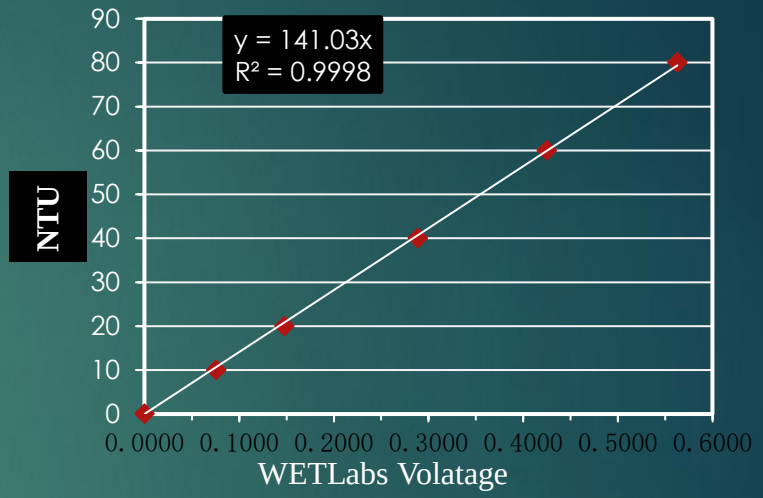


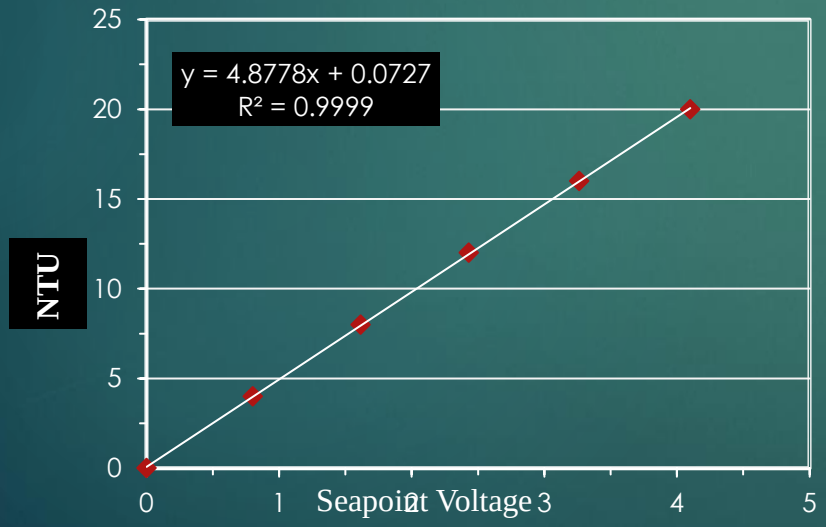
Indication Error and Repeatability

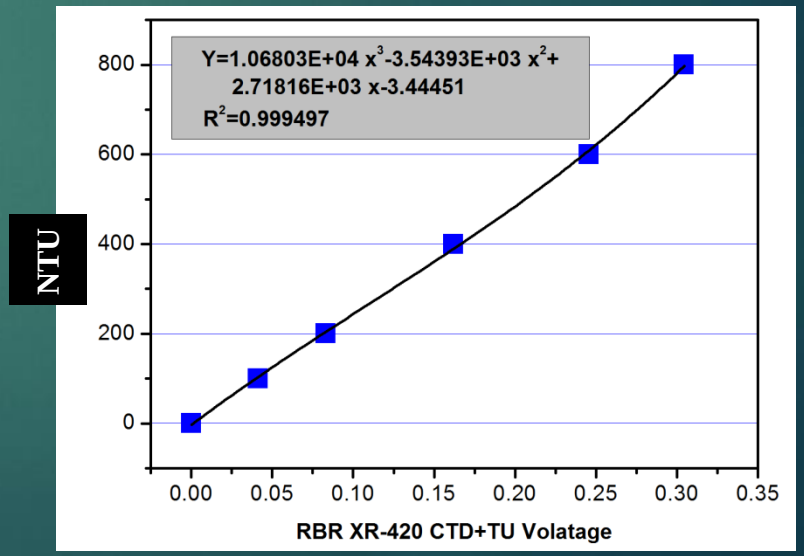


2.3 Calibration of Turbidity Sensors

- Measuring range of turbidity sensors are respectively (0~25)NTU, (0~125)NTU, (0~500)NTU, (0~1000)NTU ,etc.
- When measuring range is greater than 750, it is a curve.
- When measuring range is less than 750, it is a straight line.

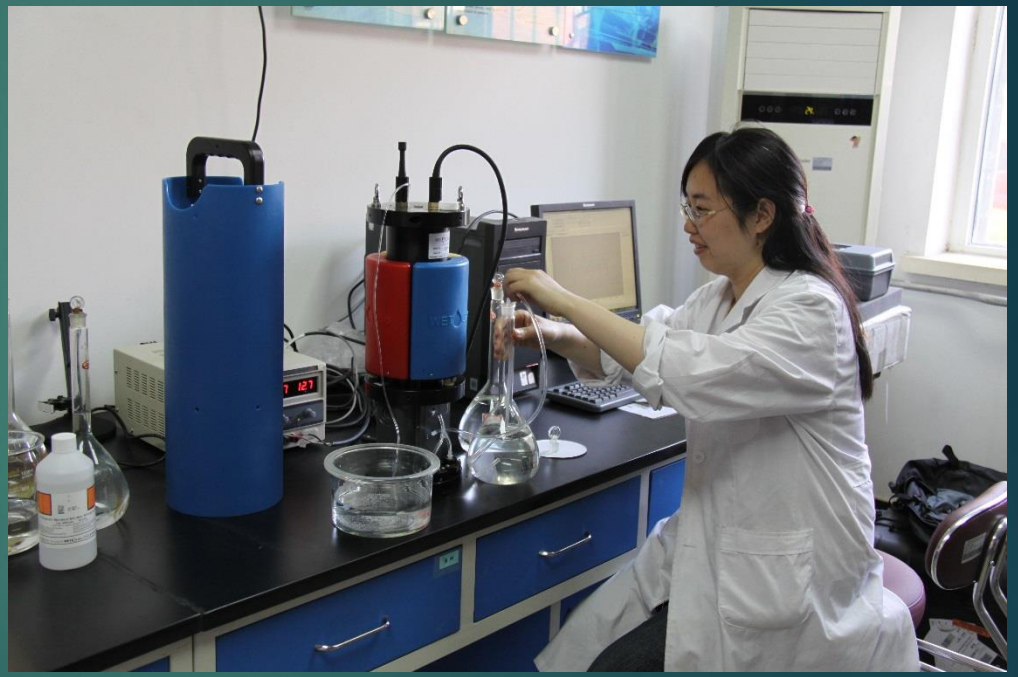






2.3 Calibration of Seawater Nutrients Analyzers

- **Temperature effect**: ignore
- **Nutrient standard solution**: provide standard value



3. Standard Materials

For chemical parameter testing, standard material is also a special and effective equipment.

- Salinity Standard Seawater
- Seawater pH_T Standard material
- Active Phosphate Standard material in seawater

3.1 Salinity Standard Seawater

Name	Number	Salinity	Uncertainty
China Primary Standard Seawater	GBW 13150	35	U=0.001（k=2）
China Series Standard Seawater	GBW（E）130011	5，20，30，35，40	U=0.003（k=2）

3.1 Salinity Standard Seawater

Comparison results between China Primary standard seawater and International Standard Seawater

Batch of China Primary Standard Seawater	Batch of International Standard Seawater	Absolute value of salinity difference	En
P7	P153	0	0
P8		2	0.14
P9	P155	4	0.28
P10		1	0.07
P11		2	0.14
P12		2	0.14
P13	P158	0	0
P14	P160	0	0
P15		6	0.42
P16		4	0.28
P17	P161	3	0.21
P18		2	0.14

3.2 Seawater pH_T Standard material

- pH_T in seawater is defined as the pH scale of total hydrogen ion concentration of seawater.

$$[H^+]=[H^+]_F\ (1+S_T/K_s)$$

$$\approx[H^+]_F+[HSO_4^-]$$

$$pH = -\log_{10}\ \left(\frac{[H^+]}{mol\ kg^{-1}\ \text{solution}}\right)$$

- Used: Seawater acidification

  Study on marine carbon cycle

  Calibration of seawater pH Analyzers based on Spectrophotometry

3.2 Seawater pH_T Standard material

- Seawater pH standard material is based on **artificial seawater** and Tris as buffer reagent.It is determined by potentiometric methods with hydrogen electrode silver / silver chloride electrode in non-liquid junction cell.

$$\mathrm{Pt(s)}\left|\mathrm{H_2(g,}\,p^0\mathrm{)}\right|\mathrm{BH^+\ and\ B\ in\ seawater}\left|\mathrm{AgCl(s)}\right|\mathrm{Ag(s)}\left|\mathrm{Pt(s)}\right.$$

cell potential：

$$E = E^\circ - \left(\frac{RT}{F}\right)\ln\left\{\frac{m(\mathrm{H^+})\,m(\mathrm{Cl^-})}{(m^\circ)^2}\right\} - \left(\frac{2RT}{F}\right)\ln\gamma_{\pm}(\mathrm{HCl})$$

After derivation

$$\mathrm{pH}_m = -\log\left\{\frac{m^*(\mathrm{H^+})}{m^\circ}\right\} = \frac{E - E_m^*}{RT\ln 10/F} + \log\left\{\frac{m(\mathrm{Cl^-})}{m^\circ}\right\}$$

$$\mathrm{pH_T} = \mathrm{pH_m} - \log(1 - 0.00106S)$$

（From Dickson A.G，1998）

Standard material（S=35）

Component	Ionic Strength	Cl^- Concentration
NaCl	0.77531	0.38766
Na_2SO_4	0.17562	——
KCl	0.02116	0.01058
$MgCl_2$	0.32844	0.10948
$CaCl_2$	0.06450	0.02150
tris（C4H11NO3）	——	——
tris·HCl	0.08000	0.04000
Total	0.72252	0.56922

3.2 Seawater pH_T Standard material

Name	Number	Value		Uncertainty
		T(℃)	pH_T	
Seawater pH_T Standard material **(Salinity 35)**	GBW(E) 130705	10	8.581	*U*=0.005, *k*=2
		15	8.414	
		20	8.250	
		25	8.092	
		30	7.937	
		35	7.785	
Seawater pH_T Standard material **(Salinity 25)**	GBW(E) 130704	10	8.566	*U*=0.005, *k*=2
		15	8.401	
		20	8.241	
		25	8.086	
		30	7.934	
		35	7.786	

Seawater pH_T Standard material

3.3 Active Phosphate Standard material in seawater

3.3 Active Phosphate Standard material in seawater

Name	Concentration（μmol/L）	Uncertainty（μmol/L）
Active Phosphate Standard material in seawater	0.50	0.05
	1.00	0.05
	2.00	0.10
	4.00	0.14

Spectrophotometric determination

4. Research in future

Thanks for listening !