

工學碩士 學位論文

**A Study on the Development of a High Accuracy
Dissolved Oxygen Measuring System using Polarographic Method**

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2001年 2月

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Abstract

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A Study on the Development of a High Accuracy Dissolved Oxygen Measuring System using Polarographic Method

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Abstract

Dissolved oxygen in pure water supplied to power plant may cause corrosion of piping arrangements, condensers or turbine's blades. For preventing accidents from corrosion, therefore, it is essential to measure the concentration of Dissolved oxygen in real-time.

In this paper we present a method of measuring dissolved oxygen very accurately up to ppb units. This method, called polarographic method, is based on the measures of the electric current generated by the oxidation process in cathode and deoxidation process in anode, assuming that the amount of the current is proportional to the density of dissolved oxygen. We introduce algorithms for the compensation of temperature and atmospheric pressure to reduce measuring errors and multiple amplification ratio algorithm to amplify small current.

Effectiveness of the suggested method is verified through a series of experiments in the real power plant field.

1

가 ,

.

· ,

가

.

,

, 가

가

.

ppb

.

,

[16].

가

.

.

.

,

(,)

.

, ppb

.

. ppm
 [6].
 winkler , (iodin metry),
 [15]. winkler
 winkler
 . 가
 .
 [2][6],
 ppb
 가 , ,
 가 가 [7].
 .
 (polarographic) .
 ,
 가 [3].
 가 ,
 가 가

. 2

, 3

,

. 4

.

5

.

2

2.1

2.1.1

(dissolved oxygen)

가

Henry¹⁾

$$P_o = H \times X_o \quad \text{-----} \quad (1)$$

P_o

, X_o

mol

, H

henry

가

2.1.2

(Ag)

(Au)

(KCl, KBr, KOH)

[2].

700mV 800mV

가

(

)

O₂

1) Henry :



).



2.1

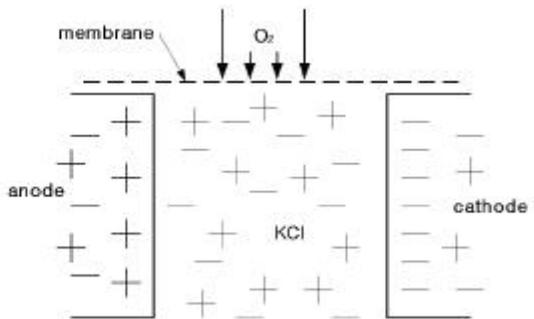
KCl
(anode)
가

가

(membrane)

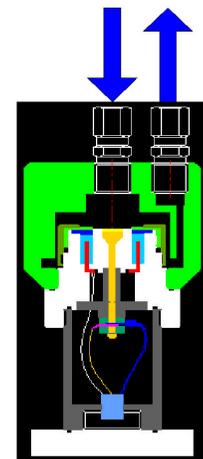
(cathode)

가



2.1a

Fig. 2.1a Dissolved oxygen measuring via electro-chemical reaction



2.1b

fig. 2.1b measuring sensor

2.2.1

(cathode)

(anode)

(reflon)

가

가

가

가

가

가

[5]

2.2.2

ppb

가

가

가

가

[1][3].

가

가

(가 μA),
가 .

2.2.3

. 가 (fouling) 가
4 5 6
[7]. ppb
, 가 .
ppm .

2.3

가 , , ,

ppb

: 0 8000 ppb

: $\pm 1\%$

: $\pm 0.5\text{ppb}$

: +0 +45

OUTPUT: 0 5V(1 5V) or 4 20mA, RS-232 or RS-485

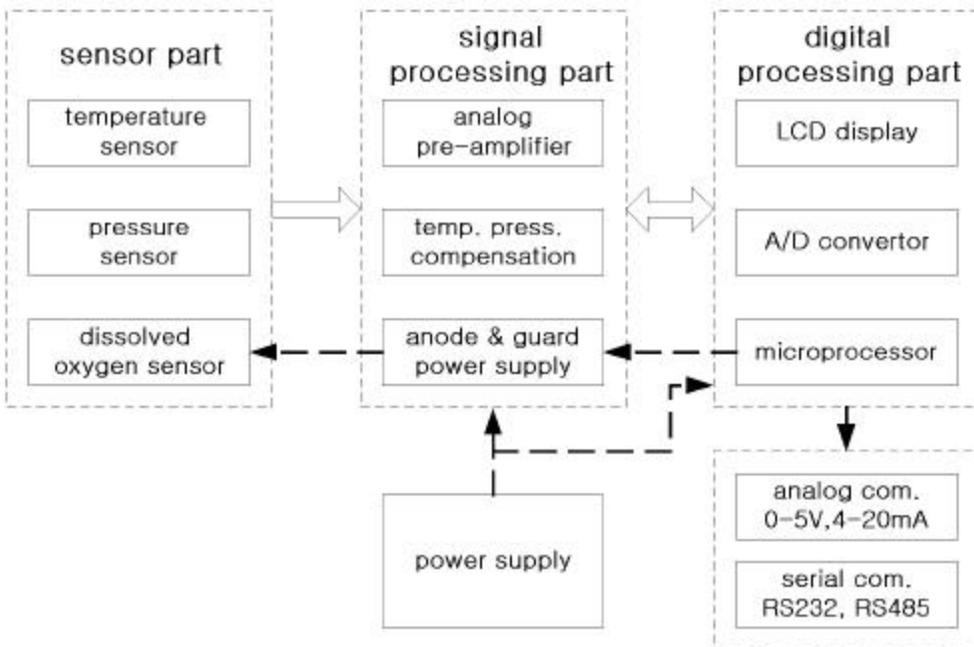
: / , , ,

가 ,

μA μA 가 .

0.4mV 가

2.3



2.3

Fig. 2.3 Diagram of measuring system

3

3.1

H/W

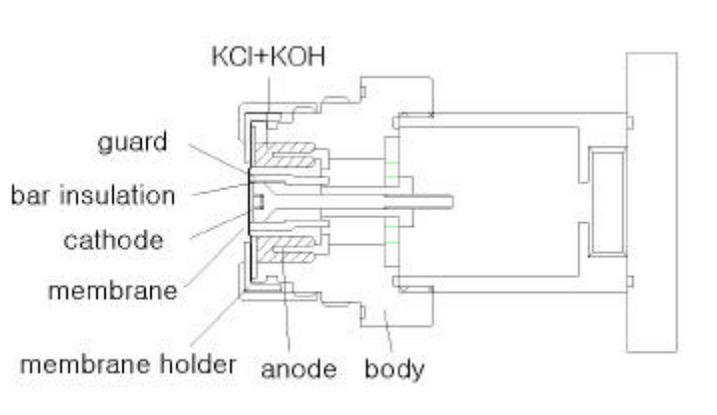
3.1.1

3.1

(anode)

(cathode),

가 (guard)



3.1

Fig. 3.1 Structure of dissolved oxygen measuring sensor

anode

cathode

, cathode

가

anode

가
 anode
 anode Ag
 3% Al
 (3.1).
 cathode
 가 ,
 [3].

가 (H₂S)
 100% (Au) cathode
 1mm
 (3.2).



3.1 Anode
 Photo. 3.1 Anode unit



3.2 Cathode
 Photo. 3.2 Cathode unit

Anode

Anode

1 KCL

[4].

[3]

가

가 .

25 μ m

가 PTFE

가 .

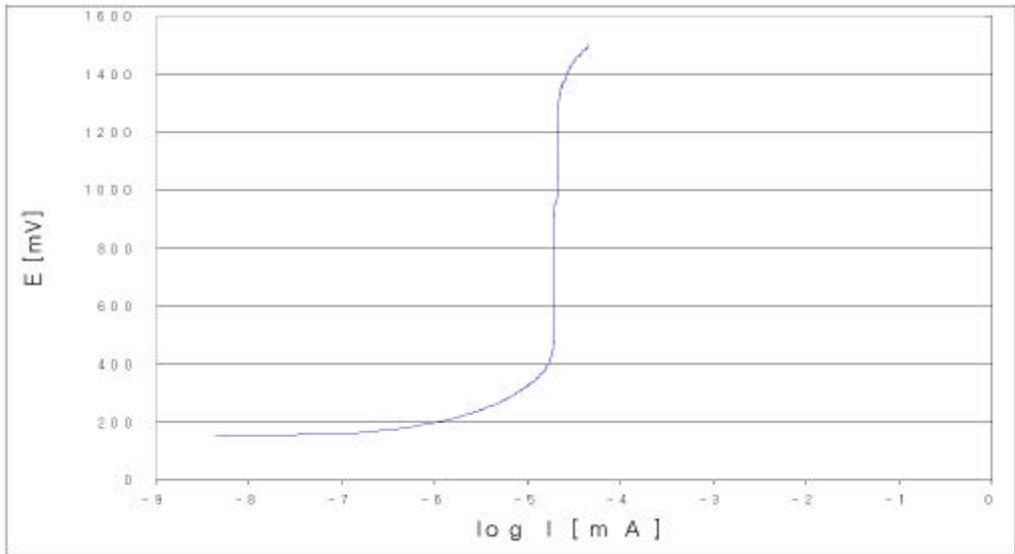
가

MC(nylon)

()

PP(polypropylene)

(cathode)



3.2

Fig. 3.2 Voltage and current characteristics of sensor

3.2

500 900mV

가

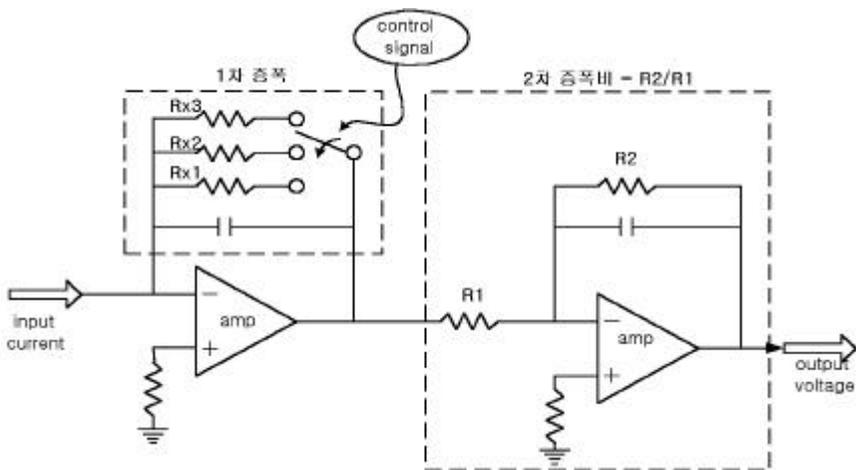
3.1.2

가
 가 0 가
 가 AD549 [11][12]. ultra-low
 50pA OP 10nA 1/500
 가 , 1015Ω

3.3

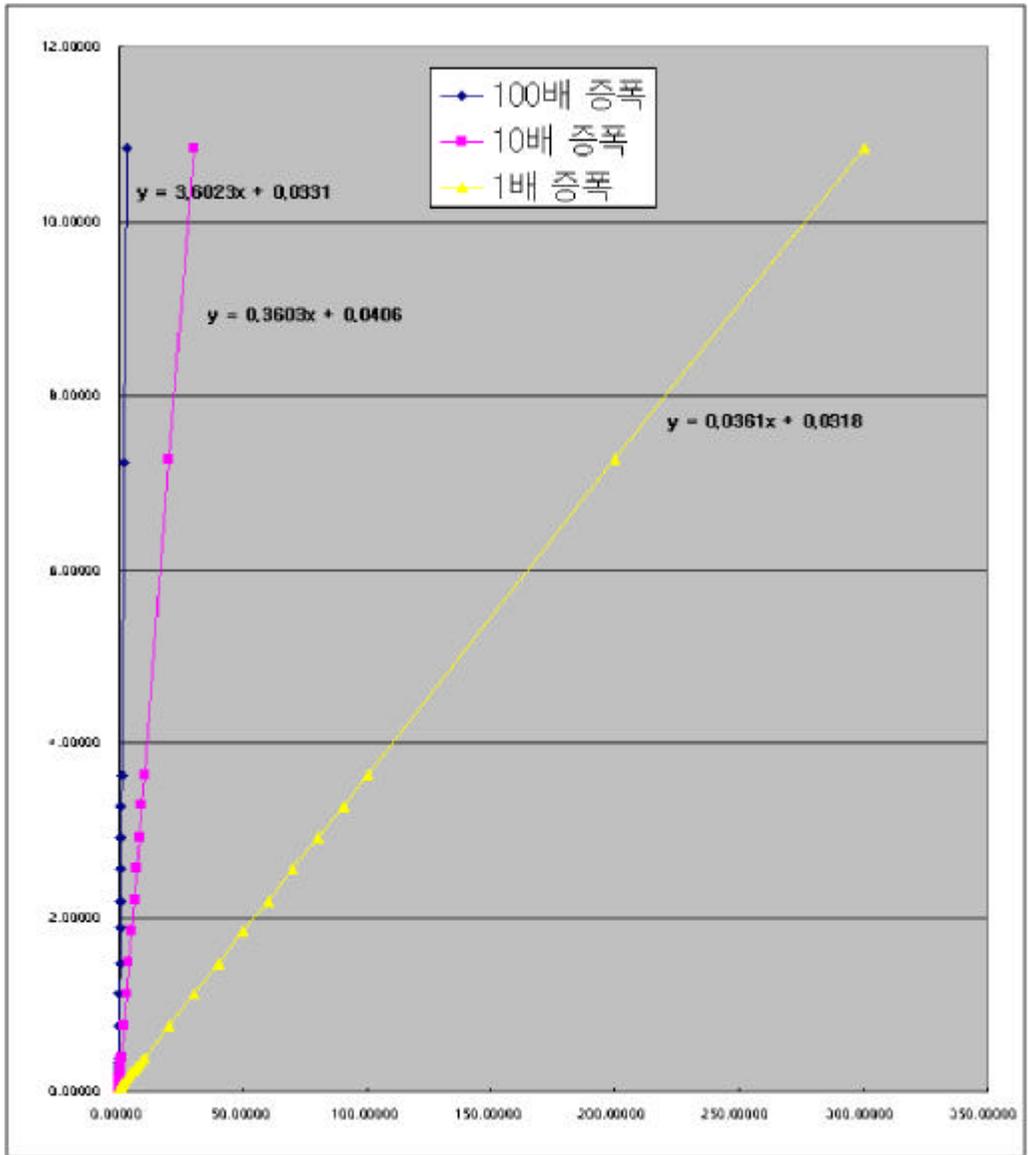
가

AD



3.3

Fig. 3.3 A little current amplification diagram of sensor



3.4

Fig. 3.4 Multiple amplification ratios according to input signal levels

3.4

가

10

가

가 10

가

(thermistor)

CPU

가

가

-25

+100

가

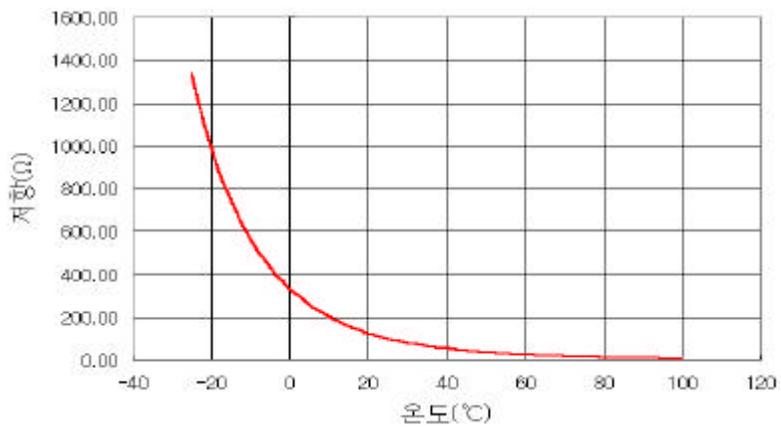
3.5

0

45

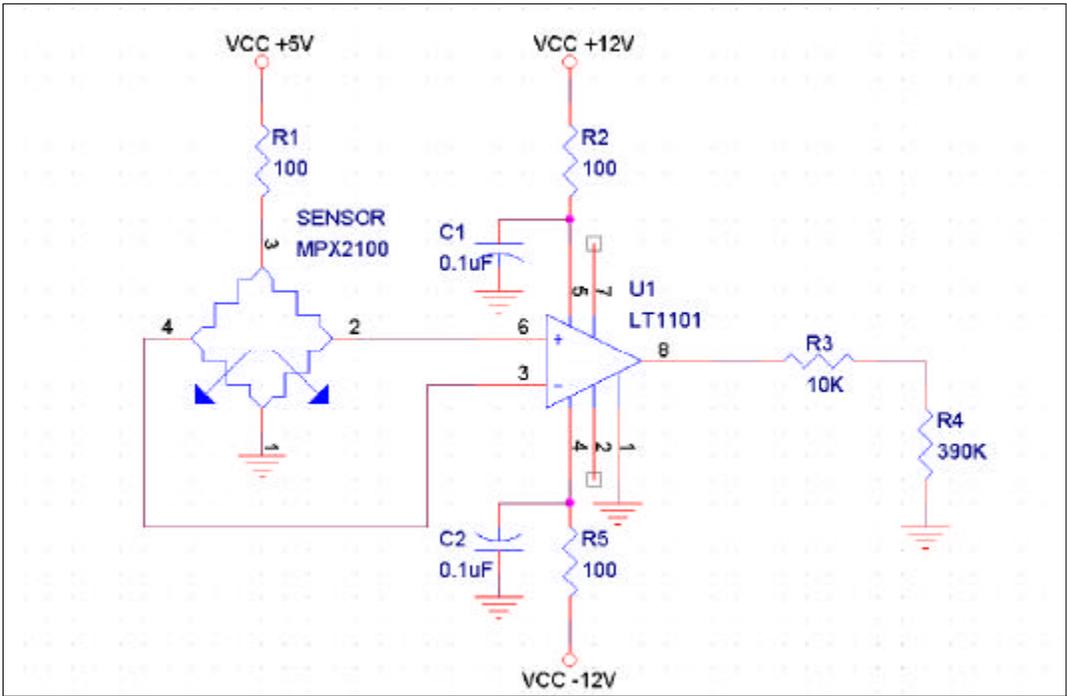
가

가



3.5

Fig. 3.5 Temperature sensor output resistance value



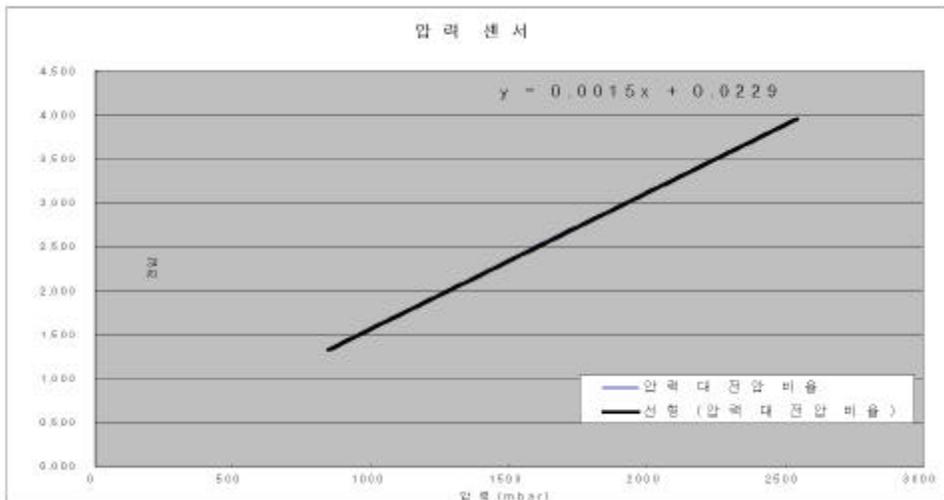
3.6
Fig. 3.6 Air pressure sensor circuit

MPX2100A 3.6
100 3.1
가 . 3.
7 . 100mBar
0.15mV .
mbar CPU .

3.1

Table 3.1 Air pressure sensor test data

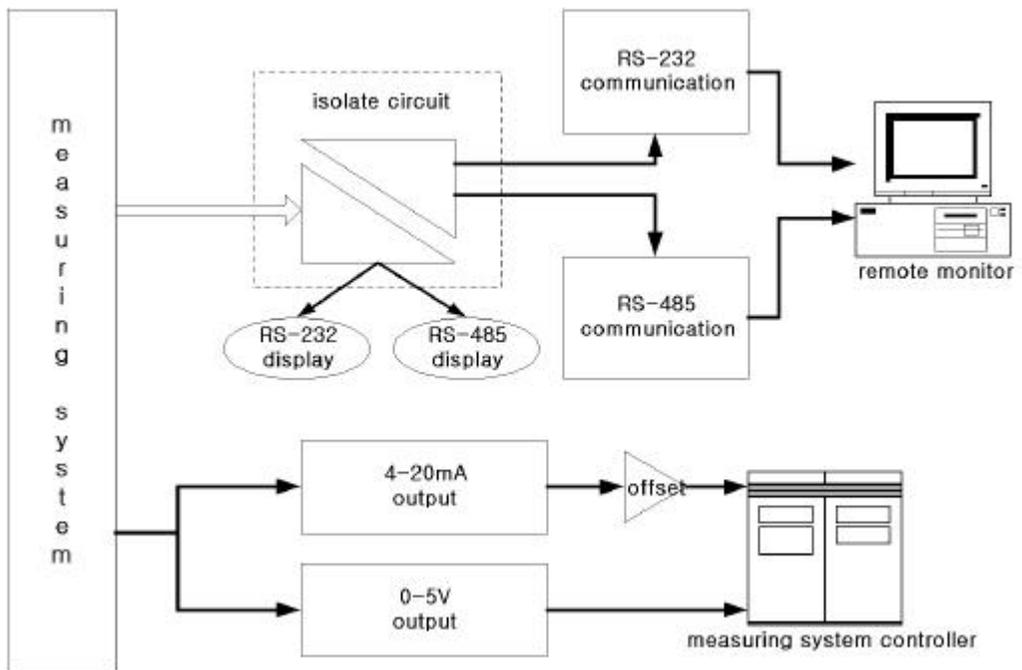
Kpa	mBar	mV		mV	
		C		C	
- 20	846	1.317			
- 10	946	1.477	0.160	1.487	1.487
0	1046	1.637	0.160	1.645	0.158
10	1146	1.795	0.158	1.807	0.162
20	1246	1.954	0.159	1.966	0.159
30	1346	2.110	0.156	2.125	0.159
40	1446	2.270	0.160	2.283	0.158
50	1546	2.423	0.153	2.441	0.158
60	1646	2.581	0.158	2.590	0.149
70	1746	2.737	0.156	2.755	0.165
80	1846	2.891	0.154	2.912	0.157
90	1946	3.042	0.151	3.066	0.154
100	2046	3.196	0.154	3.220	0.154
110	2146	3.345	0.149	3.369	0.149
120	2246	3.499	0.154	3.525	0.156
130	2346	3.649	0.150	3.676	0.151
140	2446	3.797	0.148	3.826	0.150
150	2546	3.950	0.153	3.976	0.150



3.7

Fig. 3.7 Air pressure sensor test graph

RS232
 MAX232 IC
 RS232 IC TTL
 RS232 IC가
 RS485 IC TTL
 SN75176 IC 3.8
 LED
 RS485 IC TTL
 SN75176 IC 3.8
 4 20mA, 0 5V
 가 , 가 가



3.8

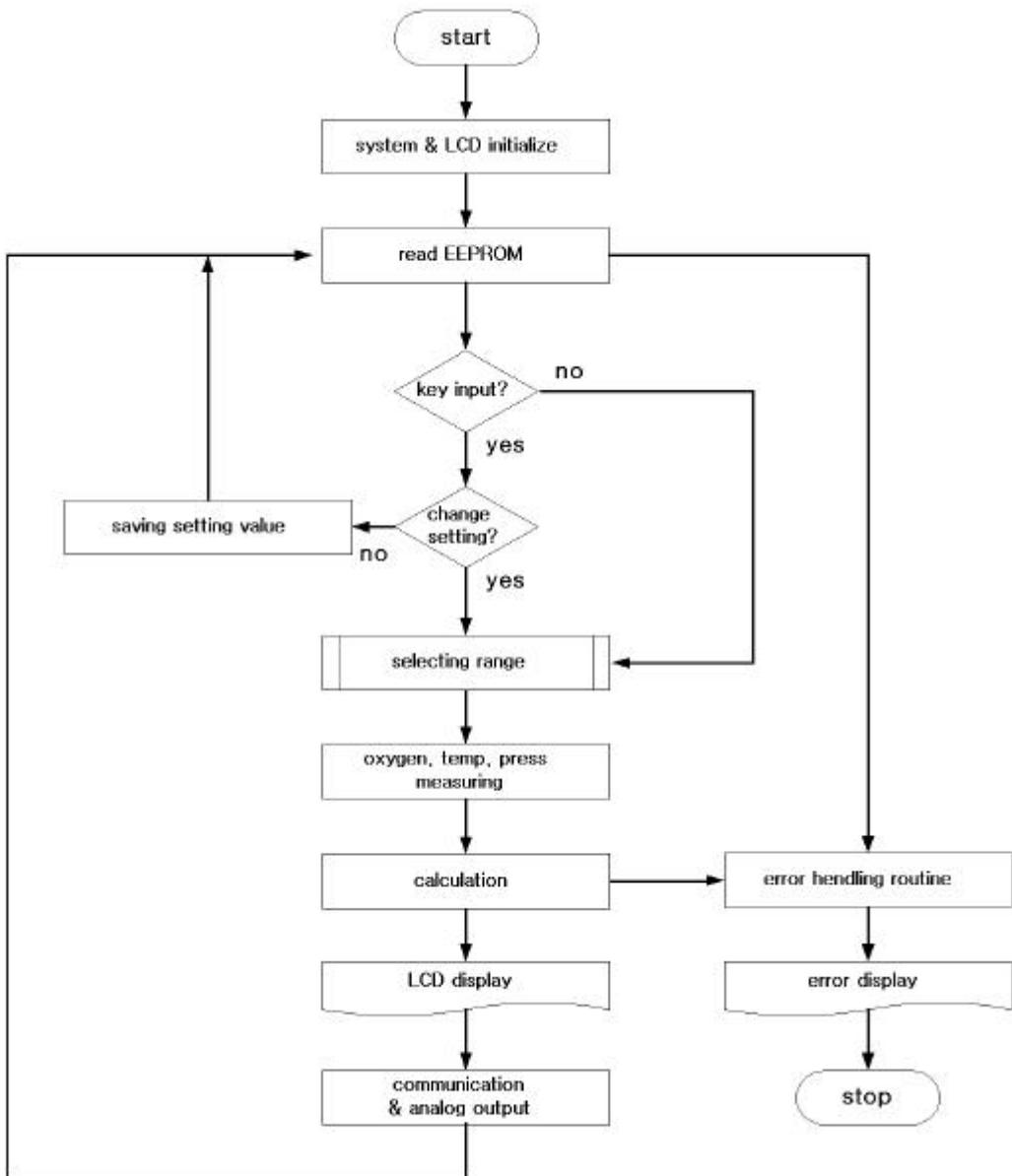
Fig. 3.8 Block diagram of digital and analog communication module

3.2

S/W

3.2.1

· ,
, ,
,
·
·
, LCD,
,
(, ,)
· , EEPROM
·
·
가 , ,
가
, 가 1 ,
5mb
, RS232 RS485, 0 5V(1 5V)
4 20mA . 3.9
·



3.9

Fig. 3.9 Flow chart of the proposed system

0 V , 0
 ppb 가 0 ppb

3.2

가

3.2

Table 3.2 Menu items of proposed system

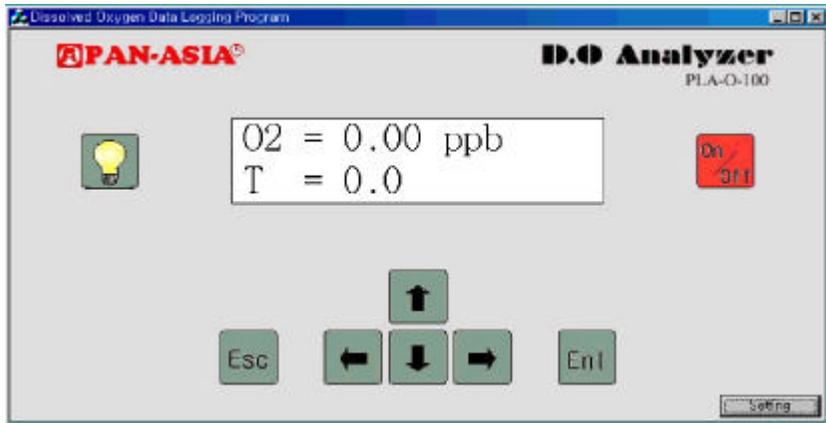
measure	measuring mode	
calibration	calibration in air	calibration detect
		calibration state
	zero voltage	vol. 00.000V
option	modify options anode volt set	vol. 000mV
	modify options guard volt set	vol. 000mV
	modify options alarm limit	dissolved oxygen limit 000ppb
	modify options digital output	RS-232 RS-485
	modify options analog output	0 5V, 1 5V 4 20mA
	modify options rolling average	rolling average disable 3 5 7 9

RS232

가 (3.10).

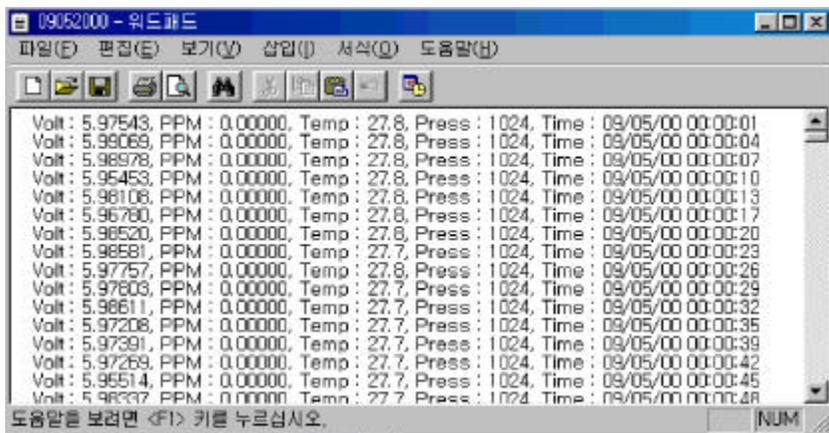
PC

(3.11).



3.10

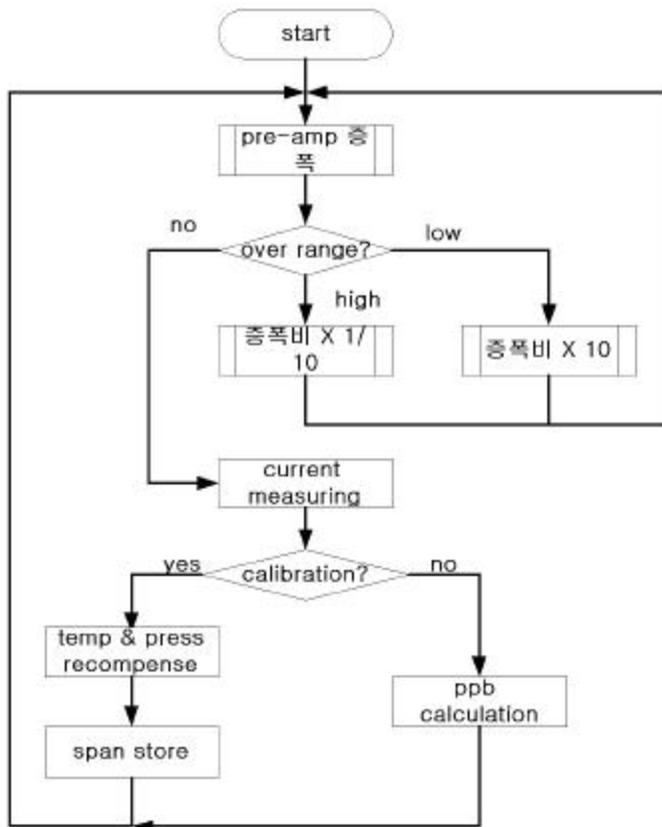
Fig. 3.10 Remote monitoring



3.11 PC

Fig. 3.11 Dissolved oxygen value measured in PC

3.1.2



3.12

Fig. 3.12 Measuring algorithm

가

가

3.12

A/D

0.5 5V

, 0.5V 10

0.3V 100k Ω

, 10k Ω 10

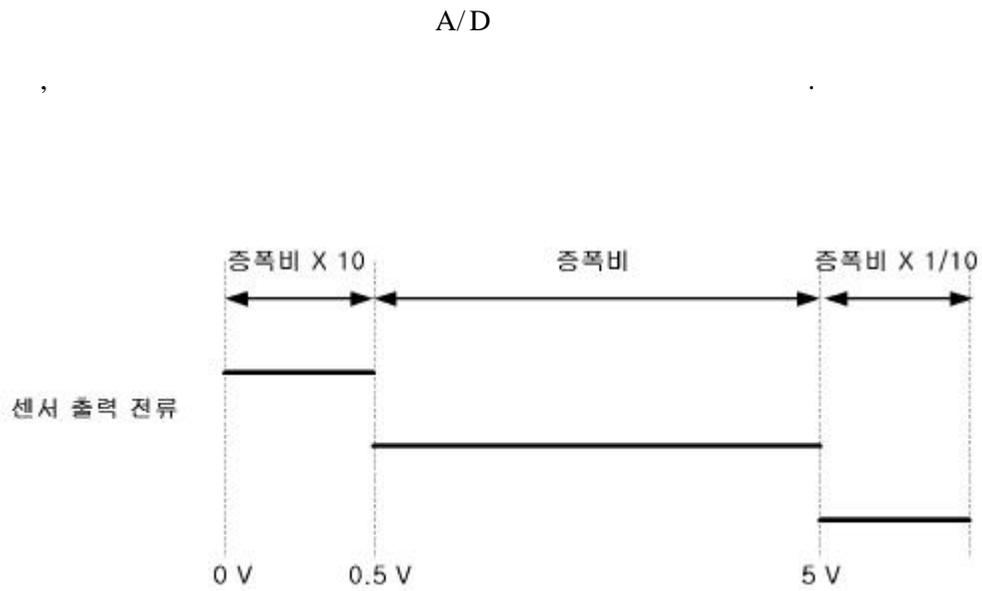
3V 10

0.5V 100

1M Ω 10k Ω

100

3.13



3.13

Fig. 3.13 Range of amplification ratio

4 가

4.1

4.1.1

K B

2 ,

가 O (-Orbisphere)

O (-Orion) 가

[13][14]. 4.1 4.2 .

4.1 1 (K)

Table 4.1 Specification of first subject experiment engine

	1	2	3 , 4
(MW)	587	650	950 × 2
	6 5	6 4	7
	가		
	(2 4%)		
	()		
	G.E.C()		

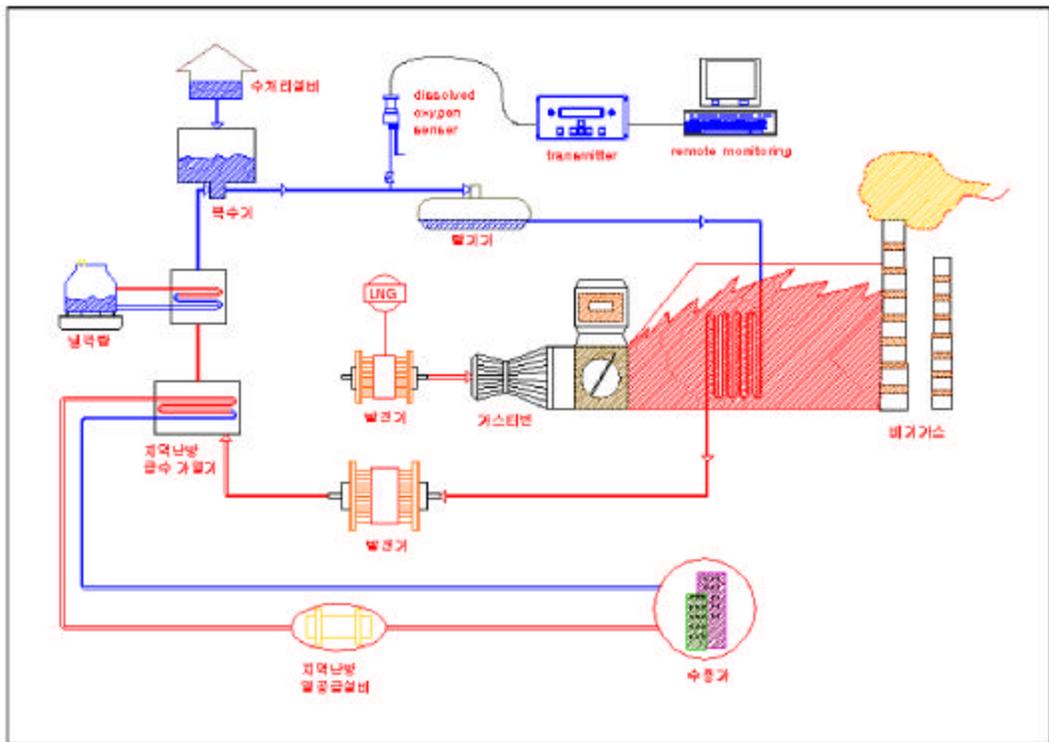
4.2 2 (B)

Table 4.2 Specification of second subject experiment engine

	G1	G2	G3, G4, G5	S1
(MW)	75	75	75 × 3	185
	93 10 19			
	가			
	가 LNG 가			
	ABB			

4.1.2

4.1



4.1

Fig. 4.1 Organization diagram of an experiment subject system

4.2

1

4.2.1 1

4.2 K

1

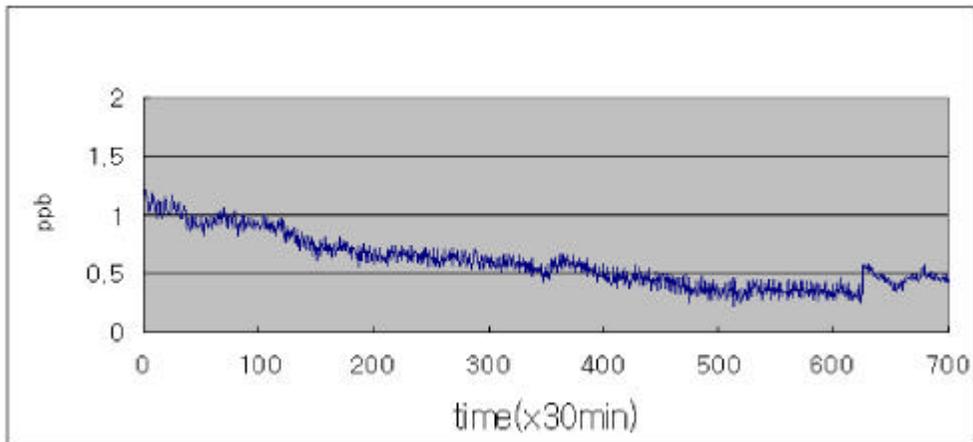
1

. 15

O ()

0.9ppb

MC(nylon)



4.2 1

15

Fig. 4.2 Test result of first experiment for 15 days

4.2.2 2

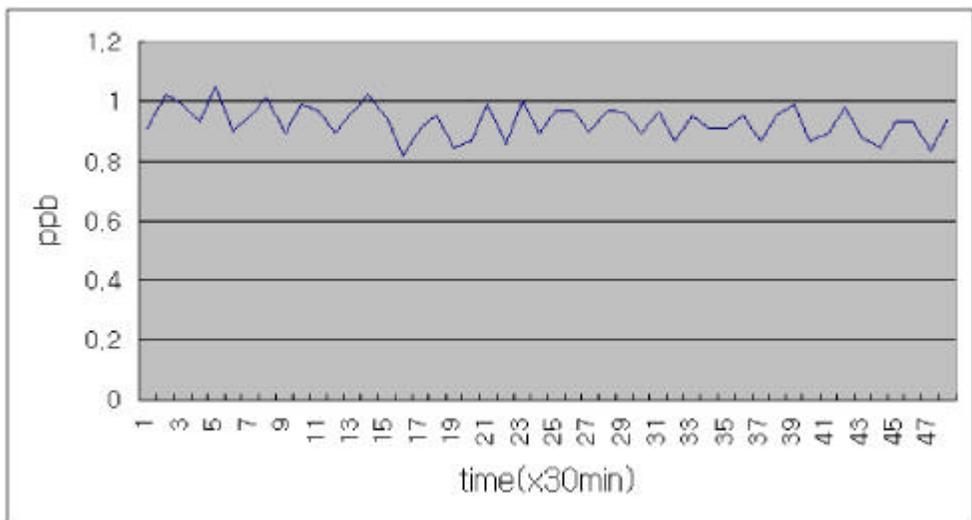
PP

O ()

0.9ppb

0.1ppb

wave가



4.3 1 1

Fig. 4.3 Test result of first experiment for one day

4.3

2

4.3.1 1

2 B 1 가

O ()

1

가

2

4.3.2 2

2

가

4.4

가 가

가

O ()

60ppb

,

50ppb

가

가

1

K

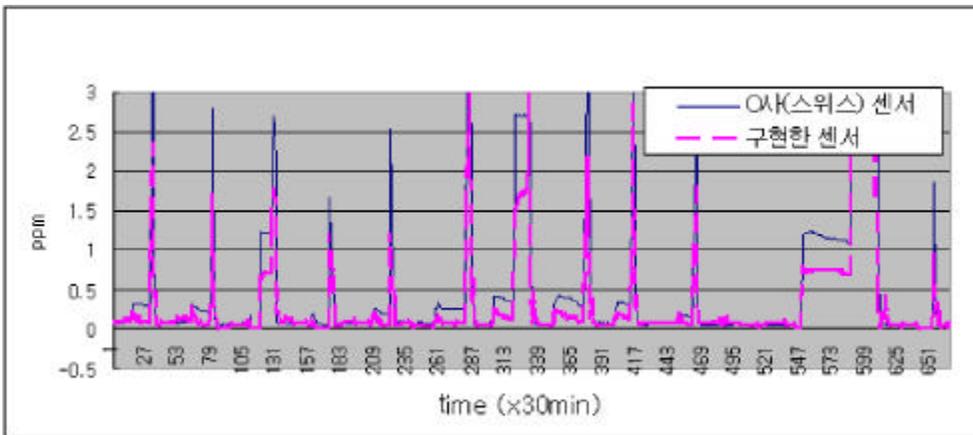
2

가

1

PP

가



4.4 2

15

Fig. 4.4 Test result of second experiment for 15 days

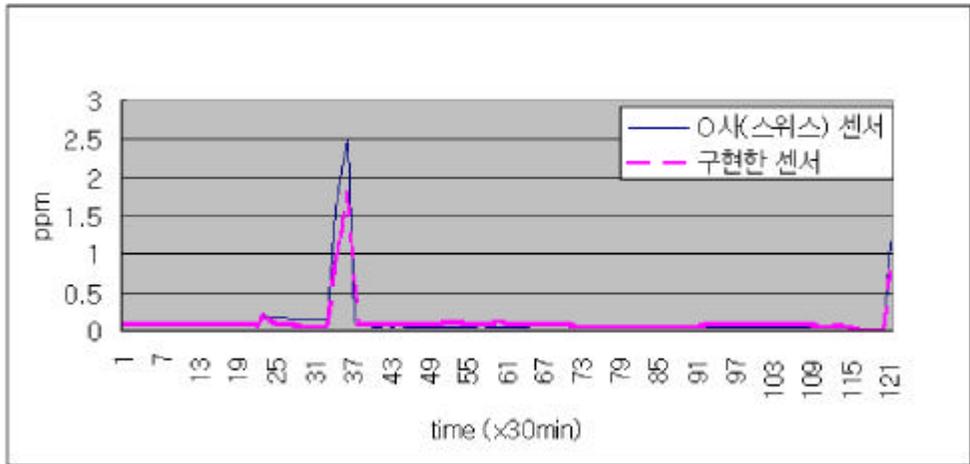
4.5 2

B

가

60ppb

O ()



4.5 2 4

Fig. 4.5 Test result of second experiment for 4 days

4.4 가

O (), R (-Rosemount)

O ()

[. 6]

[Table. 6] Comparison of dissolved oxygen measurement systems

	O	R	
range	0 20000 ppb	0 50/ 100/ 200 ppb	0 8000 ppb
accuracy	± 1%	± 1%	± 1%
response time	90% in 7.2sec(25)	90% in 20sec	90% in 30sec
sample temp.	0 50	0 44	0 45
max. pressure	20bar	3.45bar	10bar
sample flow	180Ml/ min	250Ml/ min	180Ml/ min
output	0 5V DC 0/4 20mA RS232/485	0 1/5/ 10V DC 0/4 20mA	0 5V(1 5V) DC 4 20mA RS232/485 High/Low Alarm
dimension	221.5 × 132.5 × 195(mm)	257 × 235 × 300(mm)	245 × 130 × 175(mm)
case classification	IP65, NEMA4	NEMA4	IP65

5

가 ± 1%

O

가

가

R

Ag(OH)₂

가

(AVT)

(OT)

가

- [1] 3, "DO Meter", , , 1987.
- [2] J.P. Hoare, "The Electrochemistry of Oxygen," Interscience, New York, 1968.
- [3] D.P. Lucero, "Design of Membrane-Covered Polarographic Gas Detectors," Vol. 41, APRIL, 1978.
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- [14] Rosemount Analytical model 7001D Oxygen monitors, Rosemount 7001D model Manual.
- [15] http://my.netian.com/~pdhan/2_6/do.htm.
- [16] “ , ” , , 1999.



Appendix 1. A photograph of sensor



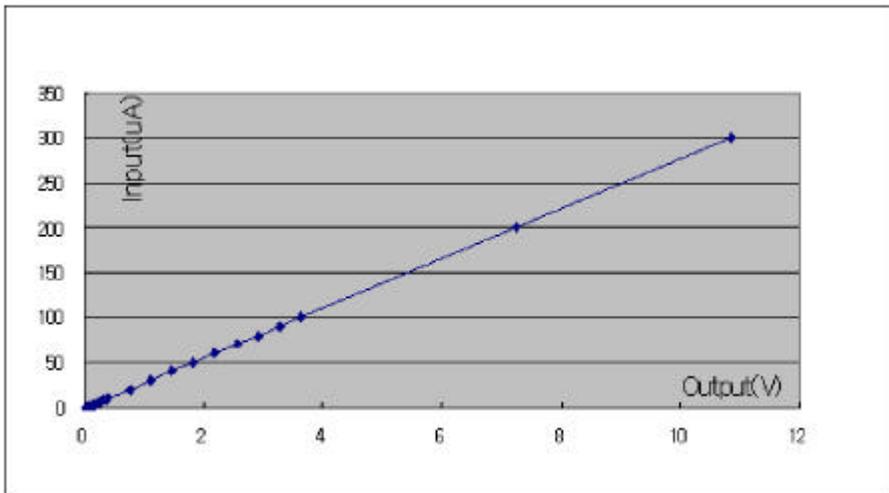
Appendix 2. Fixed of membrane



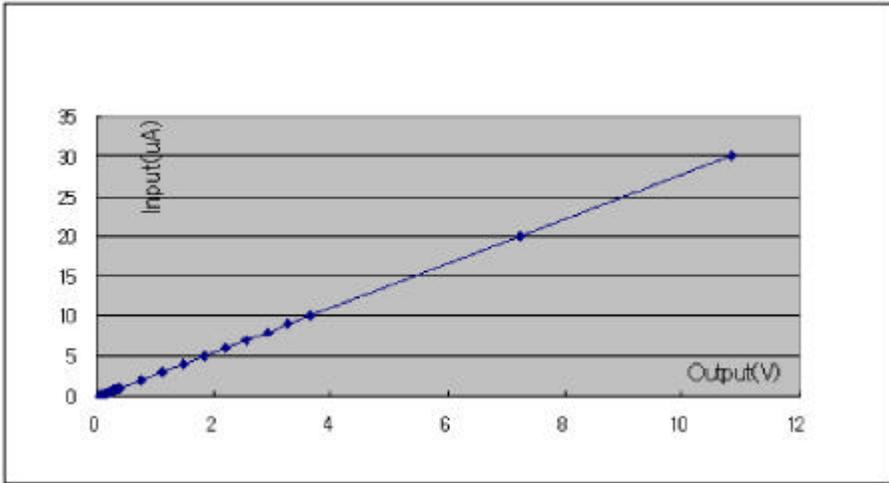
Appendix 3. Temperature and pressure sensor



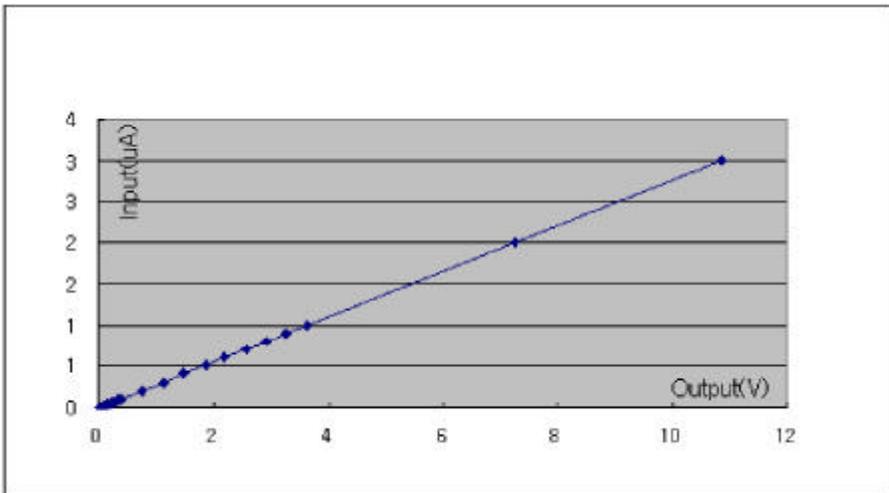
Appendix 4. Dissolved oxygen measuring system



Appendix 5. Free amplify



Appendix 6. 10 times amplify of free amplify



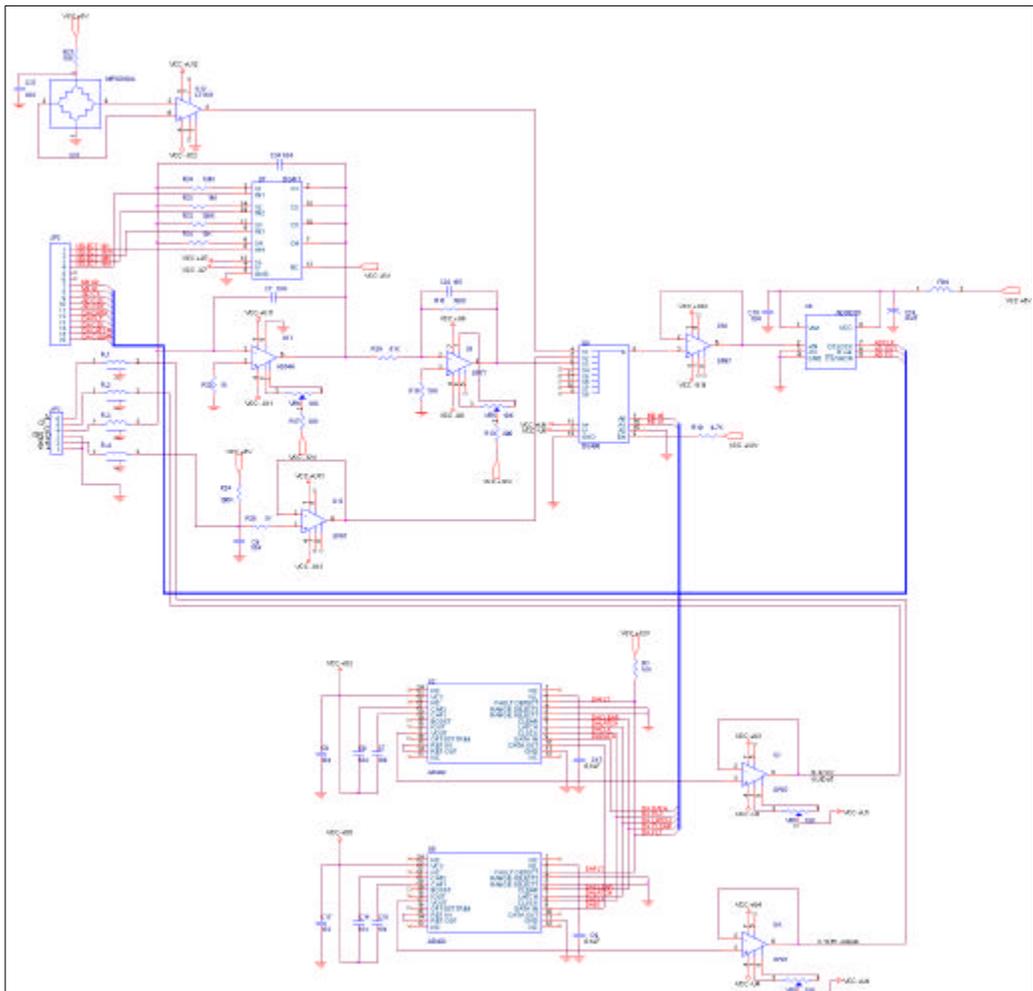
Appendix 7. 100 times amplify of free amplify

: uA	10MΩ	1MΩ	100kΩ	10kΩ
0.00005		0.03220		
0.00010		0.03240		
0.00020		0.03280		
0.00030		0.03320		
0.00040		0.03350		
0.00050		0.03390		
0.00060		0.03430		
0.00070		0.03460		
0.00080		0.03500		
0.00090		0.03530		
0.00100		0.03570	0.04140	
0.00200		0.03930	0.04180	
0.00300		0.04290	0.04210	
0.00400		0.04650	0.04250	
0.00500		0.05010	0.04280	
0.00600		0.05370	0.04320	
0.00700		0.05730	0.04350	
0.00800		0.06090	0.04390	
0.00900		0.06450	0.04430	
0.01000		0.06810	0.04460	0.03250
0.02000		0.10410	0.04820	0.03280
0.03000		0.14010	0.05180	0.03320
0.04000		0.17620	0.05540	0.03360
0.05000		0.21210	0.05900	0.03390
0.06000		0.24820	0.06260	0.03430
0.07000		0.28420	0.06620	0.03460
0.08000		0.32020	0.06980	0.03500
0.09000		0.35620	0.07370	0.03540

Appendix 8. Multiple amplification test data

: uA	10M Ω	1M Ω	100k Ω	10k Ω
0.10000		0.39220	0.07700	0.03570
0.20000		0.75300	0.11300	0.03930
0.30000		1.11300	0.14900	0.04290
0.40000		1.47300	0.18500	0.04650
0.50000		1.88300	0.22100	0.05010
0.60000		2.19300	0.25700	0.05370
0.70000		2.55300	0.29200	0.05730
0.80000		2.91300	0.32800	0.06100
0.90000		3.27300	0.36490	0.06460
1.00000		3.63300	0.40090	0.06820
2.00000		7.23000	0.76100	0.10390
3.00000		10.84000	1.12100	0.13950
4.00000			1.48100	0.17580
5.00000			1.84100	0.21190
6.00000			2.20100	0.24820
7.00000			2.56100	0.28380
8.00000			2.92100	0.32000
9.00000			3.28100	0.35620
10.00000			3.64100	0.39180
20.00000			7.25000	0.75300
30.00000			10.85000	1.11400
40.00000				1.47400
50.00000				1.83400
60.00000				2.19500
70.00000				2.55500
80.00000				2.91500
90.00000				3.27600
100.00000				3.63600
200.00000				7.25000
300.00000				10.85000

Appendix 9. Multiple amplification test data



Appendix 11. Circuit of analog part

. 3

가

가