

IN SITU DETERMINATIONS OF pH IN SOME LAKES

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pH has been determined in some lakes by using an *in situ* technique. pH has also been measured in the usual way in the field and in the laboratory. These measurements, together with the determinations *in situ*, made it possible to get information about changes of pH in the water samples during sampling, measuring, and storage. The microstratification of pH has also been investigated by means of *in situ* determinations.

pH changes in the field in water samples from different lakes have been observed. This phenomenon gave me the idea of trying to determine the pH in some lakes by measurements *in situ*.

Four lakes were chosen for these measurements. One of these lakes (Øvre Heimdalsvatn) has been investigated in connection with a fresh water project started by the Norwegian Committee of the International Biological Programme. The author was engaged as scientist in this fresh water project. The other three lakes chosen are located around Oslo, and these lakes differ from Øvre Heimdalsvatn and from each other.

Two of the four lakes (Sandtjern and Øvre Heimdalsvatn) are also treated in papers concerning hydrography (Grøterud 1971 a) and ice analyses (Grøterud 1971 b).

METHODS

pH in situ was determined by means of a glass electrode (G 2022 C) and a reference electrode (K 4022) from Radiometer, specially made for submergence,

and a Radiometer field pH meter 29. Pressure, as far as these determinations are concerned, should not influence the electrodes according to Bates (1964).

Water samples were taken with a Ruttner water sampler.

pH in the field (measurement in water samples from different depths) was determined with the two above-mentioned electrodes, and also with an ordinary combined Radiometer electrode for control and a Radiometer field pH meter 29.

pH in the laboratory (measurement in water samples from different depths, about 5 hours after sampling) was determined by means of the combined electrode and the pH meter mentioned above.

Calibration in the field was done somewhat differently depending on the purpose of pH determination *in situ*. This calibration procedure is mentioned in connection with the treatment of the measurements.

The analyses of the lake waters are not mentioned here, but they are treated in another paper (Grøterud 1971 a).

All determinations were done when the lakes were ice-covered.

RESULTS

Lake Övre Heimdalsvatn

Övre Heimdalsvatn is a high mountain lake situated in the Jotunheimen area 1,090 m above sea level. The hydrography of the lake is, as previously mentioned, treated in another paper (Grøterud 1971 a), but some facts can be reported here. The lake water is poor in lime and the total electrolyte content is low (χ_{18} is approximately 15 $\mu\text{S}/\text{cm}$). The buffering capacity (alkalinity) as mg HCO_3/l is approximately 7 and the content of oxidizable organic matter expressed as KMnO_4 consumption is ca. 3 mg/l. During winter, Övre Heimdalsvatn develops a clinograde oxygen distribution (i.e. decrease of the oxygen concentration from the surface and downwards in the lake) with accumulation of salts, especially iron, in the deep water.

The field stations where the pH measurements were done are shown on the bathymographical map, Fig. 1.

The first pH measurements were made at position L-2, and the results are shown in Table 1. As Table 1 shows, pH is determined *in situ*, in the field, and in the laboratory. The purpose of these determinations was first of all to get an impression of possible pH changes of the lake waters during the sampling-measuring process and during storage. But the intention was also to investigate the microstratification of pH in the deep waters.

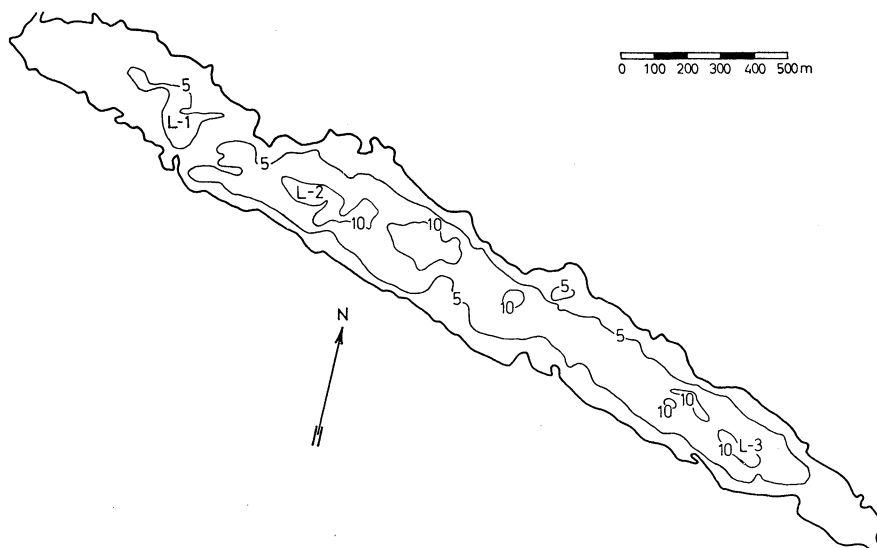


Fig. 1.

Bathymographical map of Övre Heimdalsvatn. Isobath interval 5 m. The field stations are marked with L and Arabic numerals.

The calibration was done indirectly by means of the lake's surface stratum. The pH of this surface stratum was first determined by means of the usual combined electrode. The surface stratum was then used as calibration liquid for the electrodes intended for measurement *in situ*. During the measurements *in situ*, it was often necessary to hoist up the electrodes to the surface of the lake (the calibration liquid) for a re-calibration.

The results in Table 1 indicate relatively great changes of pH in the waters from Övre Heimdalsvatn during sampling-measuring and storage. It is reasonable to suppose that the pH of the waters in Övre Heimdalsvatn first of all is dependent upon the $\text{CO}_2\text{-HCO}_3$ system, or the ratio HCO_3/CO_2 . This ratio will increase if the CO_2 content (or the CO_2 pressure) decreases, and the result is an increase of pH. This phenomenon seems to be involved in the pH changes of the water samples from Övre Heimdalsvatn except close to the lake bottom. Lake waters come under new conditions with respect to temperature and gas pressure after sampling and storage. This process could probably release CO_2 from the water samples in Övre Heimdalsvatn and in that way increase the pH values.

Table 1.

pH determinations *in situ*, in the field, and in the laboratory from Ø. Heimdalsvatn. pH found in the surface water in the field is used as calibration value for the *in situ* electrodes (Station: L-2. Date: 1 March 1970).

Depth (m)	pH <i>in situ</i>	pH field	pH lab.
0	6.33 (calibr.)	6.33	6.38
1	6.33	6.33	6.38
2	6.05	6.12	6.32
4	5.84	6.02	6.20
6	5.74	5.95	6.24
8	5.73	5.85	6.08
10	5.70	5.76	6.05
11	5.90	5.84	6.01
11.5	6.19	5.94	6.04
11.6	6.40	-	-
11.7	6.65	-	-
11.8	6.85	-	-
11.9	7.05	-	-
12 (ooze)	7.35	-	-

In the deep waters an additional process seems to occur. The HCO_3 content could decrease (and the CO_2 content increase) because of oxidation of ferrous iron which probably exists as a bicarbonate. The HCO_3/CO_2 ratio could therefore decrease during the sampling-measuring process and, accordingly, increase the acidity. The pH values from 11.5 m depth indicate this development. During the sampling and the determination in the field both the CO_2 and HCO_3 content decreased, but HCO_3 decreased more rapidly than CO_2 and therefore the water increased in acidity. The CO_2 content decreases because of pressure change, and the HCO_3 decrease is due to oxidation of ferrous iron. The latter process also gives more CO_2 to the water, and in that way counteracts the CO_2 decrease mentioned above. Kjensmo (1967) mentioned that pH decreased from 6.9 to 5.9 during an experimental determination in the field. The water was taken from the monimolimnion (i.e. the water mass that does not take part in the annual turnover) of a meromictic (i.e. the circulation extends only to a certain depth) lake and the determination lasted 10 minutes. Kjensmo supposed that the change in pH was due especially to oxidation of ferrous iron which was present in high amounts in the water.

Regarding the pH values from 11.5 m depth (Table 1), the development dur-

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ing storage (between determining pH in the field to pH in the laboratory) shows that the increase of CO₂ in relation to HCO₃ during the sampling-measuring process does not continue, but comes to a stop and then decreases.

The pH measurements in the deep water with respect to the microstratification show that the dichotomous stratification (i.e. a pH increase due to salts released from the sediments (Yoshimura 1932)) is very pronounced towards the sediment surface.

The results in Tables 2, 3, and 4 give first of all an impression of the pH stratification, especially the microstratification, at different places in the lake. In addition, some pH changes during sampling-measuring and storage are also clarified. It should not be necessary to give any further comments on these results in addition to what has been previously mentioned in connection with the results in Table 1. But some comments may be made about the calibration procedure. As already mentioned, the purpose of these measurements was primarily to get information about the pH microstratification in relation to the pH macrostratification in the lake, and therefore waters from depths close to the microstrata were chosen as calibration liquids. On these calibration liquids (water) from different depths pH was determined in the usual manner in the

Table 2.

pH determinations *in situ*, in the field and in the laboratory from Ö. Heimdalsvatn. pH found at 10 m depth in the field is used as calibration value for the *in situ* electrodes (Station: L-2. Date: 2 April 1970).

Depth (m)	pH <i>in situ</i>	pH field	pH lab.
0	—	6.48	6.48
1	—	6.48	6.48
2	—	6.16	6.50
4	—	6.03	6.29
6	—	6.06	6.19
8	—	5.98	6.16
10	5.92 (calibr.)	5.92	6.03
11	6.20	6.04	6.20
11.5	6.80	6.46	6.57
11.6	6.96	—	—
11.7	7.10	—	—
11.8	7.23	—	—
11.9	7.38	—	—
12 (ooze)	7.53	—	—

Table 3.

pH determinations *in situ* and in the field from Ø. Heimdalsvatn. pH found at 7 m depth in the field is used as calibration value for the *in situ* electrodes (Station: L-1. Date: 2 April 1970).

Depth (m)	pH <i>in situ</i>	pH field
0	—	6.47
1	—	6.47
2	—	6.26
4	—	6.02
6	—	6.02
7	6.00 (calibr.)	6.00
7.5	6.06	6.02
7.6	6.18	—
7.7	6.22	—
7.8	6.35	—
7.9	6.50	—
8.0 (ooze)	6.60	—

Table 4.

pH determinations *in situ* and in the field from Ø. Heimdalsvatn. pH found at 9 m depth in the field is used as calibration value for the *in situ* electrodes (Station: L-3. Date: 2 April 1970).

Depth (m)	pH <i>in situ</i>	pH field
0	—	6.45
1	—	6.45
2	—	6.20
4	—	6.05
6	—	6.02
8	—	6.00
9	5.96 (calibr.)	5.96
9.5	6.10	6.00
9.6	6.23	—
9.7	6.36	—
9.8	6.49	—
9.9	6.65	—
10 (ooze)	6.78	—

field, and the values obtained were again used as references for the electrodes intended for measurements *in situ*. In other words, the *in situ* electrodes were lowered to the depths chosen for the calibration procedure and the pH meter was adjusted according to the reference values. During the pH determinations of the microstrata, there was often need for a re-calibration. This procedure was rapid and practical with the calibration method in question. All that had to be done was to hoist up the electrodes to the calibration depth and re-adjust the pH meter.

Lake Sandtjern

Sandtjern is a soft water lake situated 599 m above sea level about 60 km west of Oslo. The hydrography of the lake is, as already mentioned, treated in another paper (Grøterud 1971 a) and only a few data are presented here.

The lake water is extremely poor in lime, and the electrolyte content is low (χ_{18} is ca. 11 $\mu\text{S}/\text{cm}$). The buffering capacity or alkalinity of the lake water is also extremely low. Expressed as HCO_3 , it is ca. 1 mg/l. The organic content of the lake water measured as KMnO_4 consumption is ca. 10 mg/l. In winter, Sandtjern shows about the same oxygen and iron stratification as does Övre Heimdalsvatn. At the time of measuring, an acid melt-water stratum was developing in the uppermost part of the lake.

The two field stations where the pH measurements were undertaken are marked on the bathygraphical map, Fig. 2.

The first pH determinations *in situ* were done at station S-1, and the results are given in Table 5. The intention with these measurements was to throw light on the *in situ* pH of the lake's deep waters in relation to the pH just after the sampling procedure, and to gain some knowledge about the pH values in the bottom stratum. The calibration process was done in the same way as previously described for the results in Table 1. Regarding the results in Table 5, it does not seem necessary to give any further comments in addition to what was said about the similar pH measurements in Övre Heimdalsvatn.

Table 6 gives more data concerning the pH changes during field work (sampling-measuring) and storage. A couple of pH values from the bottom stratum are also shown. In the uppermost stratum of the lake the low pH value is probably due to melt water containing relatively large quantities of H_2SO_4 (Grøterud 1971 a). However, it is rather surprising that pH changes can occur in the water samples from this stratum. This is difficult to explain, but one or two possibilities may be given. Some adsorption of H^+ ions to the walls of the sample bottles could take place. It may also be possible that some H_2SO_3 is present in the precipitation (the snow) and, accordingly, in the melt-water stratum. The H_2SO_3 might disappear as SO_2 from the water samples during stor-

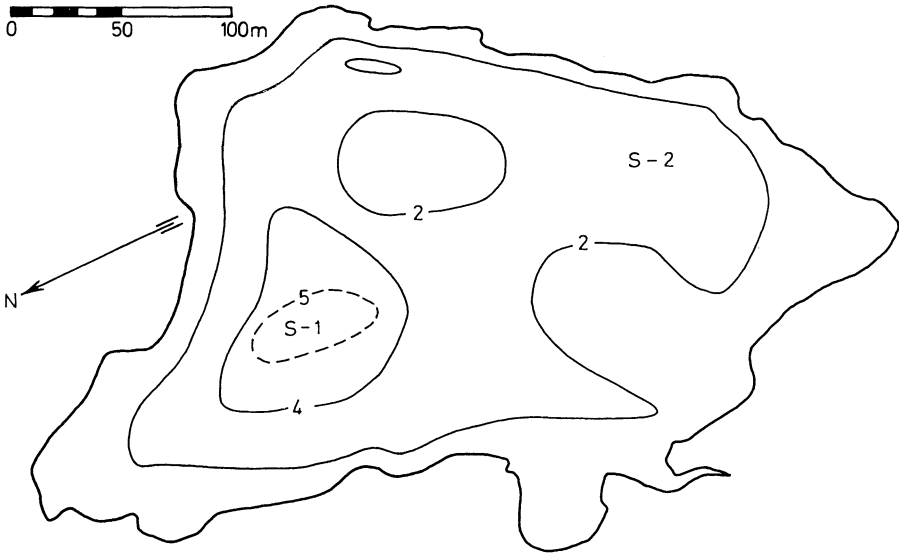


Fig. 2.

Bathymorphical map of Sandtjern. Isobath interval 2 m. The field stations are marked with S and Arabic numerals.

age (warming) and in that way increase the pH. These possibilities are rather uncertain and are open to more research.

The development of the melt-water stratum with respect to pH was inves-

Table 5.

pH determinations *in situ* and in the field from Sandtjern. pH found in the surface water in the field is used as calibration value for the *in situ* electrodes (Station: S-1. Date: 25 January 1970).

Depth (m)	pH <i>in situ</i>	pH field
0	5.30 (calibr.)	5.30
4	5.30	5.30
4.7	5.92	5.82
4.8	6.10	-
4.9	6.25	-
5	6.45	-
5.1	6.50	-
5.2 (ooze)	6.55	-

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Table 6.

pH determinations *in situ*, in the field and in the laboratory from Sandtjern. pH found in the surface water in the field is used as calibration value for the *in situ* electrodes (Station: S-1. Date: 28 March 1970).

Depth (m)	pH <i>in situ</i>	pH field	pH lab.
0	4.20 (calibr.)	4.20	—
1	4.26	4.29	4.40
3	5.25	5.28	5.39
4.7	6.25	6.19	6.20
5	6.69	—	—
5.2 (ooze)	6.87	—	—

tigated just before ice breaking. The results are presented in Table 7. The extent of the melt-water stratum in the lake was simply and rapidly determined by means of the *in situ* electrodes.

Table 7.

pH determinations *in situ*, in the field and in the laboratory from Sandtjern. pH found in the surface water in the field is used as calibration value for the *in situ* electrodes (Station: S-1. Date: 26 April 1970).

Depth (m)	pH <i>in situ</i>	pH field	pH lab.
0	3.68 (calibr.)	3.68	3.80
1	3.86	3.85	4.00
1.2	3.88	—	—
1.4	3.90	—	—
1.6	4.21	4.20	4.32
1.8	4.49	—	—
2.0	4.63	4.65	4.80
2.2	4.90	—	—
2.4	5.28	—	—
2.6	5.40	—	—
2.8	5.42	—	—
3.0	5.44	—	5.49
4	5.85	—	—
4.7	6.45	—	—
5.0	6.80	—	—
5.2 (ooze)	6.92	—	—

The results in Table 8 give information about the melt water's influence on the shallow parts of the lake.

Lake Blankvann

Blankvann is a meromictic lake situated in the Nordmarka area just north of Oslo. The lake is treated in Ström (1945) and Ström & Østtveit (1948).

The purpose of these measurements was to confirm a pH increase in a stratum between 18 and 20 m depth in the lake as described by Larsson (1971), and to observe the possible pH changes during the sampling-measuring process. The stratum in question lies between the mixolimnion (the water mass that takes part in the annual turnover) and the monimolimnion of the lake, and it contains many sulphur bacteria (the water has a slight reddish color). The calibration procedure was carried out in the same way as mentioned for Sandtjern.

According to Table 9, the pH increase in the above-mentioned stratum seems to be a reality. This pH increase is probably due to a CO₂ decrease caused by a special type of photosynthesis by the sulphur bacteria (Ruttner 1963). The pH decrease during sampling-measuring is possibly therefore a result of CO₂ supply from the atmosphere. The water sample from the monimolimnion (25 m depth) also shows a pH decrease during sampling-measuring, but this phenomenon is possibly due to a HCO₃ decrease.

Lake Langvann

Langvann is a polluted lake situated north-east of Oslo. The hydrography of the lake is indicated by an investigation done simultaneously with the pH measurements and the data are presented in Table 10.

Table 8.

pH determinations *in situ* and in the field from Sandtjern. pH found in the surface water in the field is used as calibration value for the *in situ* electrodes (Station: S-2. Date: 26 April 1970).

Depth (m)	pH <i>in situ</i>	pH field
0	3.80 (calibr.)	3.80
1	4.05	4.00
2	5.10	5.00
2.2	5.30	—
2.4	5.42	—
2.6 (ooze)	5.56	—

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Table 9.

pH determinations *in situ* and in the field from Blankvann. pH found in the surface water in the field is used as calibration value for the *in situ* electrodes (Date: 22 April 1970).

Depth (m)	pH <i>in situ</i>	pH field
0	7.55 (calibr.)	7.55
18	7.20	7.18
19	7.43	7.35
20	7.18	7.20
25	6.65	6.55

Table 10.

Hydrographical data from Langvann (Date: 7 March 1970).

Depth (m)	1	6	10
Temp., °C	0.61	3.09	3.69
χ_{18} , μS	116.0	154.1	185.0
Colour, mg Pt/l	20	60	120
KMnO ₄ , mg/l	16.00	16.70	19.80
Oxygen, ml/l	0.44	0.00	0.00
Oxygen, ‰	4.4	0.0	0.0
H ₂ S, ml/l	0.00	0.12	0.44
Ca, mg/l	10.26	15.24	16.83
Mg, mg/l	2.72	4.38	4.86
Na, mg/l	9.00	11.40	13.40
K, mg/l	2.22	3.22	5.20
HCO ₃ (A), mg/l	36.60	51.85	70.76
SO ₄ , mg/l	14.54	19.71	19.57
Cl, mg/l	9.24	13.41	20.00
NO ₃ +NO ₂ -N, $\mu\text{g/l}$	20	<5	<5
NH ₄ -N, $\mu\text{g/l}$	1690	2380	2670
PO ₄ -P, $\mu\text{g/l}$	<2	<2	<2
Fe(II+III), $\mu\text{g/l}$	250	565	1310
Mn(t.inorg.) $\mu\text{g/l}$	260	340	620
Σ anions, meq/l	1.164	1.639	2.132
Σ cations, meq/l	1.278	1.831	2.103

The results from the pH determinations are given in Table 11. As appears from the Table, the intention was to get information about the pH *in situ* in relation to the pH determined in the usual way in the field.

Regarding the results in Table 11, it seems difficult to explain the relatively great pH decreases during the sampling-measuring procedure. But pressure changes (concentration changes) of gases in the water samples are certainly involved in this phenomenon.

Table 11.
pH determinations *in situ* and in the field from Langvann. pH found in the surface water in the field is used as calibration value for the *in situ* electrodes (Date: 7 March 1970).

Depth (m)	pH <i>in situ</i>	pH field
0	6.45 (calibr.)	6.45
6	6.72	6.59
10	6.90	6.60
10.5	6.97	6.65
11 (ooze)	6.80	6.60

CONCLUSION

In view of the pH determinations from the four lakes, it seems obvious that the *in situ* pH is somewhat different from the pH measured in the usual way in the field. This difference is probably caused by pressure changes (concentration changes) of gases during the sampling-measuring procedure.

From a practical point of view, it is relatively rapid and easy to investigate the pH microstratification as well as the macrostratification in lakes by means of the *in situ* measurements. In cold weather it is difficult to carry out pH determinations electrometrically because of freezing of the electrode system. It is possible to avoid this by using the *in situ* technique.

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