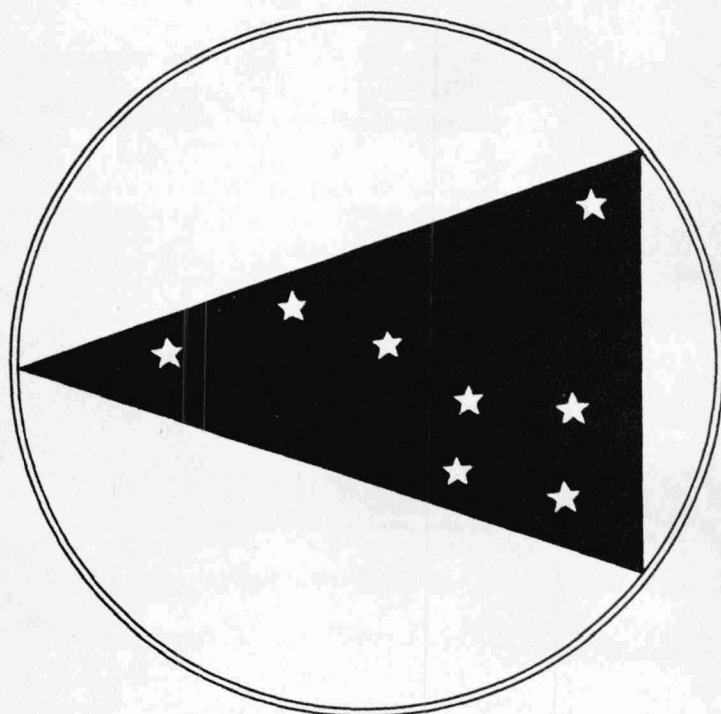


Conseil Permanent International pour l'Exploration de la Mer
Service Hydrographique
Charlottenlund Slot - Danemark



Information on Techniques and Methods for Sea-Water Analysis

No. 1



Edited by
ICES Subcommittee on Chemical
Analysis of Sea-Water

1967

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These contributions should not be
cited without prior reference to the author

Preface

Dear Colleagues,

This is the first issue of a technical information sheet from the ICES Subcommittee on Chemical Analysis of Sea-Water. The purpose of such an informal information sheet is to encourage contact between the different laboratories and groups, which are involved in marine chemistry. It should also activate exchange of experience on current work at an early state, and provoke collaboration.

Whosoever has been confronted with practical laboratory work of some kind in chemistry, knows that much practical experience is necessary to solve questions in chemical research work. Most of this experience is exchanged only if the colleagues meet and find the time to talk together, and not by means of scientific publications.

This sheet should serve as an instrument for free exchange of thoughts and experience between colleagues. The Subcommittee feels, that quite a lot of double work might be avoided if the contact between laboratories were closer. On the other hand, parallel work might be stimulated in such cases where this seems to be desirable.

Marine chemistry is an expanding science, and this implies an increase of research and survey work in this field. The methods and instruments for sea-water analysis are in a developing stage, and they are, in many cases, far from sufficient. Only practical experience and trials can show, whether new methods are suitable and represent improvements. Rapid exchange of experience on new methods and instruments, as well as of experience from intercalibration trials, shall also be among the main purposes of this sheet.

In commencing a new project, you may find the experience of colleagues of value to facilitate your work. Often efforts are wasted because of ignorance of what your colleagues are doing.

Therefore, this sheet may be an instrument for asking information and experience, if such is available, in the chemical laboratories of the ICES area.

It is planned to give short notes on current work in the different laboratories. The danger that somebody may misuse such information is small. The value of contact, on the other hand, is very great.

For the Subcommittee on
Chemical Analysis of Sea-Water

K. Grasshoff

Note. The information sheet will be issued once or twice a year. Contributions for the next issue should be sent to the member of the Subcommittee from the country in question, or directly to the Chairman of the Subcommittee. The present members of the Subcommittee are:-

Prof. E. Fjyn (Norway)
Mr. S. Fonselius (Sweden)
Dr. K. Grasshoff (Germany)
Dr. P. Jones (United Kingdom)
Dr. F. Koroleff (Finland)
Dr. F. Mosetti (Italy)
Mr. V. Olsen (Denmark)
Mr. K. Palmork (Norway)
Prof. H. Postma (Holland)
Dr. U. Stefnsson (Iceland)
Dr. A. Simonov (U.S.S.R.)

A Practical Modification of the Phosphate Analysis Method
by Murphy and Riley and the Fast Routine Work with a
Spectrophotometer on board a Ship

by

Sven Engström and Stig Fonselius
Fishery Board of Sweden, Hydrographic Department, Göteborg

Experience has shown that the single solution method by Murphy and Riley (1962) is the best and most suitable phosphate analysis method for routine work at sea.

For practical purposes some modifications of the technical work can however be introduced. Intercalibration tests (Koroleff, 1965); (Fonselius, 1966) have shown that filtering of the water is not necessary in the Baltic and North Sea areas, if sample water is used as reference solution instead of distilled water. Still better is to use sample water acidified with acid and molybdate, because the absorbance of the sample may change when reagents are added. In this way turbidity of the sample water is compensated.

The single solution recommended by Murphy and Riley is stable for only 12 hours. Therefore a new solution has to be prepared every day. If the ascorbic acid however is stored separately as suggested by Koroleff (pers. comm.), the solutions have been found to be stable for several weeks. The analysis method used at the Fishery Board of Sweden is carried out as described below:

The reagents recommended by Murphy and Riley are used in the original concentrations. All reagents except the ascorbic acid solution are mixed together and stored in a glass bottle. The ascorbic acid solution is stored separately in a dark glass bottle in the refrigerator. From each water sample 2 glass stoppered 50 ml test tubes are filled with 25 ml of sample using a Vogel pipette. To both test tubes 3.5 ml of mixed reagent is added with an automatic 5 ml DL syringe pipette (manufactured by Dansk Laboratorieudstyr A/S, 3 Ryesgade, Copenhagen N, Denmark). To the second test tube 1.5 ml of ascorbic acid is added with a similar 2 ml syringe pipette. The test tubes are stoppered and shaken and allowed to stand for at least 10 minutes and maximum 12 hours. The absorbance of the samples is measured in a Beckman B spectrophotometer at 882 m μ using 5 cm cuvettes. The water of the first ascorbic acid free test tube is used in the reference cuvette. The results are evaluated from a curve constructed by means of a standard series of phosphate samples.

For the routine work at sea the spectrophotometer has been furnished with an arrangement for fast filling and draining of sample water without removing the cuvettes from the cuvette housing. The method is applicable to most models of photometers and spectrophotometers and may be used in most kinds of routine measurements. The construction of the device

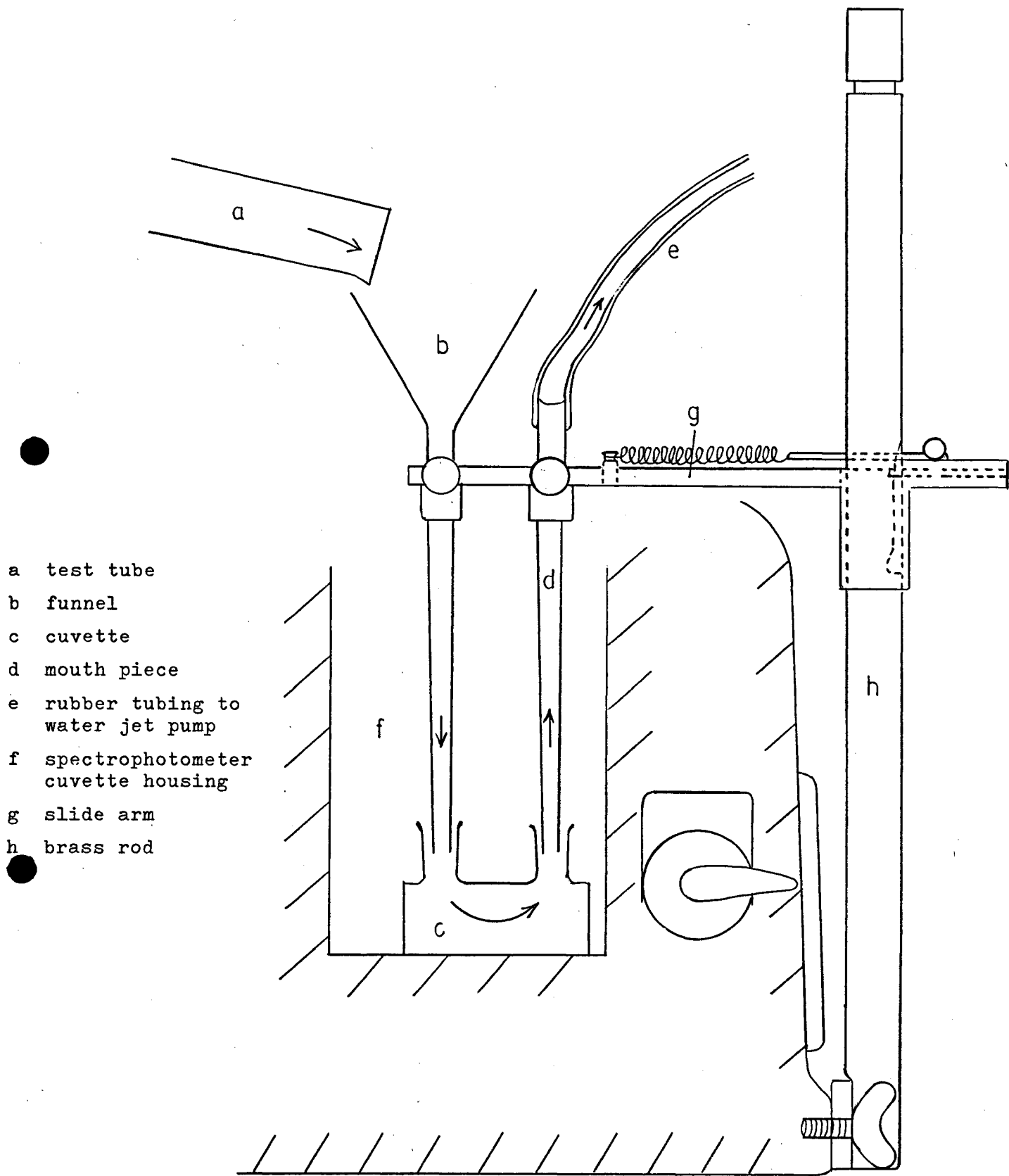
is described in detail below:

A stand made of brass (Fig. 1, h) is clamped to the base of the spectrophotometer with two screws. On the rod a sliding arm (Fig. 1, g) can be moved up and down. The arm can be locked in three positions (Fig. 2, a, b and c) by means of a spring locking device (Fig. 3 b) and jacks in the rod. The sliding arm extends over the cuvette housing (Fig. 1, f) and is fitted with two holes (Fig. 3 c and d) corresponding to the two necks of the cuvette (Fig. 1, c) when this is in the light path. Through the holes a small glass funnel and a mouth piece of glass tubing (Fig. 1 b and d) fitting through the cuvette necks, are fastened with the ends at the same height. The mouth piece is connected to a water jet pump by means of a plastic or rubber tubing (Fig. 1, e). When the slide arm is locked in its lowest position the funnel and the mouth piece extend through the necks exactly to the bottom of the cuvette. In the second position the ends extend half way into the necks (Fig. 1). In its highest position the slide arm can be turned away from the cuvette housing and the cover of the housing can be closed.

When the work begins the cover is opened, the water jet pump is put to work and the two cuvettes are placed in position in the photometer. They are stored filled with distilled water. The stoppers are removed and the slide arm is carefully lowered into its lowest position. The water is now automatically sucked out and the cuvette is washed with sample in filling through the funnel from the test tube (Fig. 1, a). Then the arm is lifted into its middle position. The rest of the sample is now flushed through the cell. The jet pump prevents the cuvette from overflowing. The arm is then lifted into its highest position and the second cuvette is moved into position. The same procedure is repeated with the test tube containing the second part of the sample. Thereafter the slide arm is turned aside, the cover is closed and the absorbance is measured in the ordinary way. The procedure is repeated with the next set of samples. The water jet pump is connected to the salt water system of the ship and is kept going during the whole analysis work. The method described allows a fast and safe handling of the samples also in rather bad weather.

References.

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Spectrophotometer with filling device

Fig. 1

- a lower jack
- b middle jack
- c upper jack

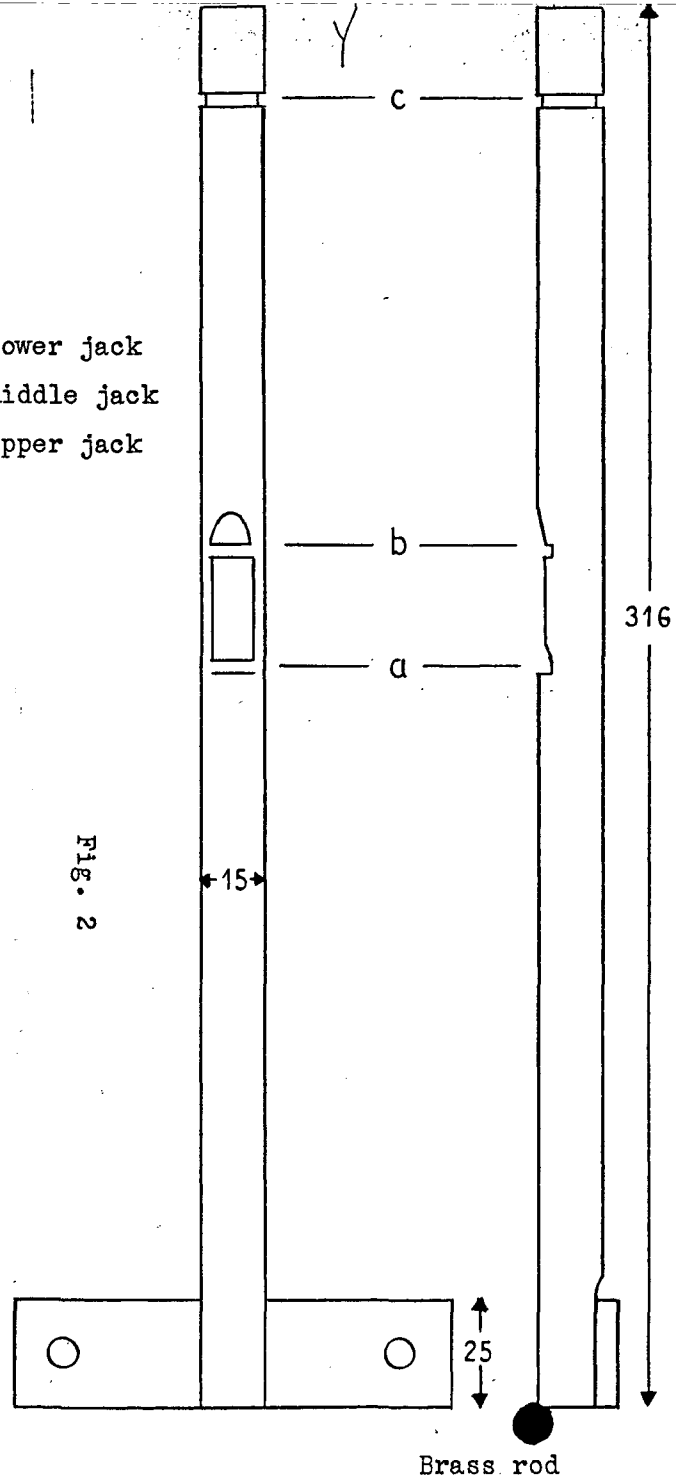


FIG. 2

- a spring
- b locking device
- c holder for mouth piece
- d holder for funnel

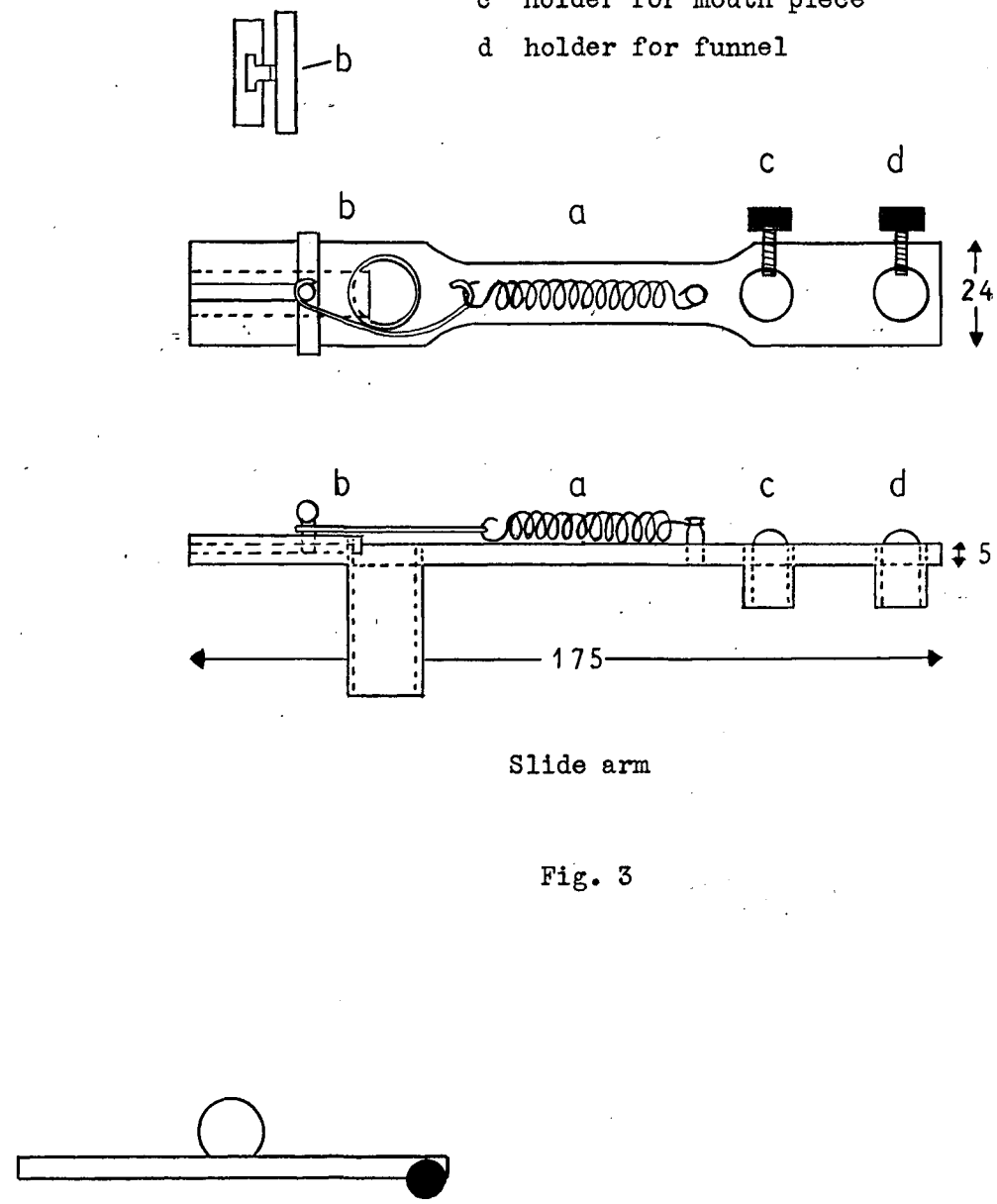


Fig. 3

The Sources of Errors in the Precise Determination
of Chloride in Sea-Water

by

G. Reusmann

Institut für Meereskunde der Universität Kiel

The concentration of chlorides in sea-water can be determined potentiometrically (F. Hermann, 1951) with high precision, and in a short time. However, the method is not quite satisfactory. From time to time wrong analytical results occur, which can be traced back to the drift in electrode potential. Therefore, several investigations have been carried out in the last few years, to indicate the equivalence point of the titration more precisely. But at present none of these methods are used in practice because they are too cumbersome or the indication of the equivalence point is not exact.

In this paper we want to point out some sources of errors which we could observe during our own work on chlorides.

The potentiometric determination of chloride in sea-water.

According to the method published by F. Hermann (1951), 99% of the chloride in sea-water is pretitrated with a strong solution of silver nitrate. After that the silver electrode is brought into this solution, and should show a potential of 50-100 mV higher than the potential of the equivalence point of the titration. But if the pretitration is carried further than this, the potential of the electrodes, which are dipped in the solution of low chloride concentration, reaches the equilibrium very slowly. In most cases the analytical results are wrong.

As is known, the surface of the silver electrode should be very clean. If it is contaminated the potential reaches a constant value very slowly and furthermore the potential may differ from that of a clean electrode. Normally the trouble can be overcome by dipping the electrode in a strong nitric acid solution.

The potential of the equivalence point should be known with an accuracy of ± 1 mV (F. Hermann). If the deviation of the equivalence potential and the determined potential is larger than this, the analytical results will still be correct on the condition that the chloride concentrations of the standard and of the sea-water sample are the same. If the difference of the chloride concentrations of the standard and of the sample increases, the resulting errors will do likewise.

Therefore, it should be possible to titrate chloride by a potentiometric method whose accuracy is independent of the error of the determination and the drift of the potential at the equivalence point. But one has to take care that standard and sea-water are titrated with equal quantities of the same silver nitrate solution. Therefore we have modified the method published by F. Hermann in such a way that we overtitrated for 1% 10 ml of the strong silver nitrate solution with the sea-water sample. Afterwards we titrated back potentiometrically with diluted silver nitrate solution according to the method described by F. Hermann. The first analytical results, which we got by this method, are quite satisfactory. We want to make a critical comparison with other methods when we have more analytical results.

Large errors may occur due to the easy adsorption and desorption of moisture on the glass walls of the reaction vessel. Also one should take care to prevent evaporation of the solutions. A suitable vessel for weighing and for the analytical determination of the sample is a flask with a narrow neck. The vessel should be covered with a lid before weighing the solutions.

The concentration of chloride in sea-water can be determined with a high accuracy, if the sea-water sample and the silver nitrate solution are measured with a suitable burette (Dean 1962, Bather and Riley 1953).

The known Knudsen burette is changed in such a manner that the graduated tube under the bulb has only a diameter of 1 mm. The burette is kept at constant temperature. The disadvantage of the method is, that a large number of burettes have to be used if determinations are to be made over a wide range of concentration. Wrong analytical results may occur, however, if the pretitration with a strong silver nitrate solution is done with one burette and the following titration with a diluted silver nitrate solution with another burette; the overall accuracy cannot be better than the accuracy of the burette which contains the strong silver nitrate solution.

Amperometric and differential potentiometric determination of chloride in sea-water.

In this section we want to discuss our own efforts to find another method for the indication of the equivalence point of the titration. If a constant potential of 10-50 mV was put over two silver electrodes which were dipped in a sea-water sample, the resulting current changes during the titration. At the equivalence point the current reaches a minimum. The accuracy of the amperometric and of the potentiometric determinations is almost the same. The disadvantage of the method is that the polarisation resistance of the electrodes depends on their surface conditions. Therefore, the shape of the amperometric curve will change very easily if the treatment of the electrode before each titration is not the same.

Reeburg and Carpenter (1964) published a method to indicate the equivalence point of the titration by means of differential potentiometry. Two equal silver electrodes are used. One is dipped in the sea-water sample, and the other is placed inside a syringe. After each addition of a few ml of a silver nitrate solution, the potential is measured.

Afterwards the sea-water inside and outside of the syringe is mixed, and the addition of silver nitrate is repeated. By means of this method the first derivative of the normal potentiometric titration is measured directly. As in the amperometric method the equivalence point is redetermined in each titration. However, it is very difficult to produce two equal silver electrodes, which reach the same constant potential in a short time and at the same rate.

We think that at present the potentiometric determination of chloride in sea-water (F. Hermann, 1951) is the most reliable and exact determination ($\pm 0.001\%$ Cl) of chloride, if one hesitates to analyse chloride by the cumbersome method of Volhard used at the Standard Sea-Water Service in Copenhagen. We shall be glad if we can exchange experiences with other laboratories doing precision chloride titrations of sea-water.

pH Measurements in Sea-Water

by

Joris M. Gieskes

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Recent trials for the intercalibration of the pH measurements in sea-water (Gieskes 1966, 1967) show that the pH method is in need of standardization. Only then comparable results will be obtained.

Strickland and Parsons (1965) describe a procedure for the measurement of the pH in sea-water. This method makes use of a low ionic strength buffer solution. Bates (1964a) pointed out that, if measurements were carried out at higher ionic strengths, the pH value is not a clearly defined quantity. Smith and Hood (1964) developed some buffer solutions of high ionic strength, i.e., the ionic strength of sea-water of 35‰. The method is rather cumbersome, and not very suitable for routine shipboard determinations. Other buffer solutions at higher ionic strength are being developed at present. For the time being, however, and especially for brackish water regions or for regions where large variations in salinity occur, the use of Bates' (1964b) standard buffer solutions is recommended. Also Palitzsch' (1916) borac-boric acid buffer solution is a very suitable buffer.

Next to the use of Bates' and of Palitzsch's buffer solutions, the measurement of pH at constant temperature should be advocated. In that case corrections can be made for deviations from ideality of the electrode system, even with relatively simple pH meters. The following procedure is recommended:(Fig. 4).

Standardize the instrument with Bates' 1:1 phosphate buffer. Then bring the electrodes into a phthalate solution, or, if an expanded range pH meter is used, Palitzsch's borax-boric acid buffer solution. If no potentiometer is available for the adjustment of " Δ pH", the temperature compensation dial can be used for these purposes. A final check on the calibration can be made with Bates' borax buffer solution. At this constant temperature the pH scale will then be well defined, so that comparable results can be obtained.

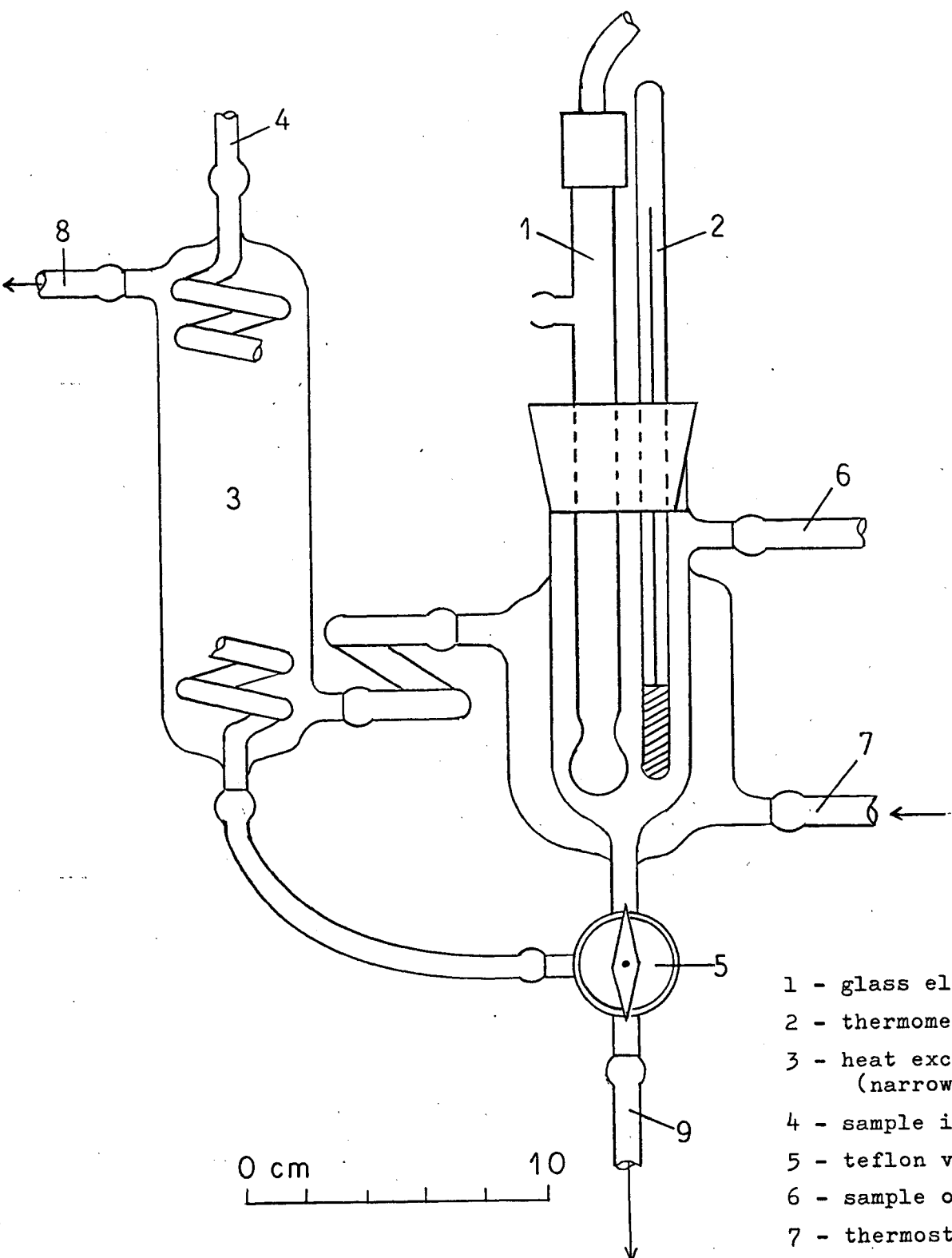
Pytkowicz et al. (1966) discuss the reproducibility of the electrometric pH determination, with particular emphasis upon the deterioration of the glass electrode. Gieskes (loc.cit.) estimated the overall reproducibility of the pH method to be ± 0.02 pH units. If, however, special precautions, such as work at constant temperature, are taken, an accuracy of ± 0.01 pH units should be attainable.

Often, after having been used for a while, the electrode system - usually a combined electrode pair - will show tendencies of drift or will only slowly reach equilibrium. In that case the employment of a fresh electrode pair is recommended rather than regeneration of the electrodes.

At present the problem of the temperature effect on the pH measurement is under reexamination in Kiel, also in connection with the method for correction for in situ pH. The use of Buch and Nynäs' (1939) method of correction is advocated. New correction factors will be calculated, using the latest data on the carbonate system. Until then, however, Buch and Nynäs' data should be used to insure comparable measuring results.

References

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- 1 - glass electrode
- 2 - thermometer
- 3 - heat exchanger (narrow bore)
- 4 - sample inlet
- 5 - teflon valve
- 6 - sample overflow
- 7 - thermostated water in
- 8 - thermostated water out
- 9 - to waste

Thermostated pH Cell
I.f.M. Kiel

A Table for Determination of Alkalinity
by the Method of Standard Acid Addition

by

K. Grasshoff

Institut für Meereskunde der Universität Kiel

The method of D.H. Anderson and R.J. Robinson (1) for the determination of alkalinity by means of standard acid addition to a fixed volume of sample and measuring the resulting pH has proved to be rapid and reliable. Especially the development of more accurate pH meters and better glass electrodes makes the determination of alkalinity by means of pH measurement more attractive. To facilitate the calculation of the resulting alkalinity, tables have been computed for waters with salinities below 30‰ and above 30‰. The values of the activity coefficients (f_{H^+}) for the hydrogen ion in relation to the total salinity have been compiled from different sources (2) (3) (4) and carefully interpolated by means of a smoothed curve. The normality of the hydrochloric acid has been taken as 0.0100. In the range from 0 - 32‰ to 40 ml of sample 10 ml of 0.0100 n HCl is added. For salinities above 32‰ the volumes are 50 ml and 15 ml. The acid is standardized against sodium tetraborate deca hydrate according to the method of F. Koroleff (see below). Otherwise the description of the procedure given by H. Barnes (2) and J.D.H. Strickland (5) is followed. To maintain an exact normality 100 ml of 0.0100 commercially available 0.1 n standard hydrochloric acid should be diluted to about 980 ml with CO₂ free distilled water, and the rest of the water should be added as calculated from the standardization. We observed in several cases that the commercially available standard acid solutions showed remarkable deviations from the stated normality (up to 1.4%).

Remark. At present work on the comparability and the possible small systematic differences between the procedures of H. Wattenberg (6) and K. Buch (3) is carried out at the Institut für Meereskunde, Kiel.

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40 ml sample and 10 ml 0.0100 n acid

S ^o /oo	3	4	5	6	7	8	9
3.00 pH	1.059	.990	.948	.926	.910	.898	.889
01	1.092	1.025	.984	.963	.947	.935	.926
02	1.123	1.058	1.017	.997	.981	.969	.961
03	1.156	1.091	1.052	1.032	1.017	1.005	.997
04	1.186	1.123	1.084	1.065	1.050	1.039	1.031
05	1.216	1.154	1.116	1.097	1.083	1.072	1.064
06	1.244	1.184	1.147	1.129	1.115	1.104	1.096
07	1.273	1.215	1.179	1.160	1.147	1.136	1.129
08	1.301	1.244	1.208	1.191	1.177	1.167	1.159
09	1.329	1.273	1.238	1.221	1.208	1.197	1.190
10	1.356	1.301	1.267	1.250	1.238	1.228	1.221
11	1.382	1.328	1.295	1.279	1.266	1.256	1.250
12	1.406	1.354	1.322	1.305	1.293	1.284	1.277
13	1.432	1.381	1.350	1.334	1.322	1.312	1.306
14	1.455	1.405	1.374	1.359	1.347	1.338	1.332
15	1.480	1.431	1.401	1.386	1.374	1.365	1.359
16	1.503	1.455	1.426	1.411	1.400	1.391	1.385
17	1.526	1.479	1.451	1.436	1.425	1.417	1.411
18	1.547	1.502	1.474	1.460	1.449	1.441	1.435
19	1.569	1.525	1.497	1.483	1.473	1.465	1.459
20	1.591	1.547	1.520	1.507	1.497	1.489	1.483
21	1.611	1.568	1.542	1.529	1.519	1.511	1.506
22	1.631	1.589	1.564	1.551	1.541	1.534	1.528
23	1.651	1.611	1.586	1.573	1.563	1.556	1.551
24	1.671	1.632	1.607	1.595	1.586	1.578	1.573
25	1.690	1.651	1.627	1.616	1.606	1.599	1.594
26	1.707	1.669	1.646	1.634	1.625	1.619	1.614
27	1.726	1.689	1.666	1.655	1.646	1.639	1.635
28	1.743	1.707	1.685	1.674	1.665	1.659	1.654
29	1.761	1.725	1.704	1.693	1.684	1.678	1.673
30	1.778	1.743	1.722	1.711	1.703	1.697	1.693
31	1.794	1.760	1.739	1.729	1.721	1.715	1.710
32	1.810	1.777	1.756	1.746	1.738	1.732	1.728
33	1.825	1.793	1.773	1.763	1.756	1.750	1.746
34	1.841	1.810	1.790	1.781	1.773	1.768	1.764
35	1.856	1.825	1.806	1.796	1.789	1.784	1.780
36	1.870	1.840	1.821	1.812	1.805	1.800	1.796
37	1.885	1.855	1.837	1.828	1.821	1.816	1.812
38	1.899	1.870	1.853	1.844	1.837	1.832	1.828
39	1.915	1.885	1.868	1.859	1.853	1.848	1.844
40	1.926	1.899	1.882	1.874	1.867	1.862	1.859
41	1.939	1.913	1.896	1.888	1.881	1.877	1.873
42	1.952	1.926	1.910	1.902	1.896	1.891	1.888
43	1.964	1.938	1.922	1.915	1.909	1.904	1.901
44	1.977	1.952	1.936	1.929	1.923	1.918	1.915
45	1.988	1.964	1.949	1.941	1.935	1.931	1.928
46	2.000	1.976	1.961	1.954	1.948	1.944	1.941
47	2.011	1.988	1.974	1.966	1.961	1.957	1.954
48	2.023	2.000	1.986	1.979	1.974	1.970	1.967
49	2.033	2.011	1.997	1.990	1.985	1.981	1.978

40 ml sample and 10 ml 0.0100 n acid

S ^o /oo	3	4	5	6	7	8	9
3.50 pH	2.045	2.023	2.009	2.003	1.998	1.994	1.991
51	2.055	2.033	2.020	2.014	2.009	2.005	2.002
52	2.065	2.044	2.031	2.025	2.020	2.016	2.013
53	2.075	2.054	2.042	2.036	2.031	2.027	2.025
54	2.085	2.065	2.053	2.047	2.042	2.038	2.036
55	2.094	2.074	2.062	2.056	2.052	2.048	2.046
56	2.104	2.085	2.073	2.067	2.063	2.059	2.057
57	2.112	2.094	2.082	2.077	2.072	2.069	2.067
58	2.121	2.103	2.092	2.086	2.082	2.078	2.076
59	2.130	2.112	2.101	2.095	2.091	2.088	2.086
60	2.138	2.121	2.110	2.105	2.101	2.098	2.096
61	2.147	2.130	2.120	2.114	2.110	2.107	2.105
62	2.154	2.138	2.127	2.122	2.118	2.115	2.113
63	2.163	2.147	2.137	2.132	2.128	2.125	2.123
64	2.170	2.154	2.144	2.140	2.136	2.133	2.131
65	2.177	2.162	2.152	2.147	2.144	2.141	2.139
66	2.184	2.169	2.160	2.155	2.152	2.149	2.147
67	2.192	2.177	2.168	2.163	2.160	2.157	2.155
68	2.199	2.184	2.175	2.171	2.168	2.165	2.163
69	2.206	2.192	2.183	2.179	2.176	2.173	2.171
70	2.212	2.198	2.189	2.185	2.182	2.180	2.178
71	2.219	2.205	2.197	2.193	2.190	2.187	2.186
72	2.225	2.212	2.203	2.199	2.196	2.194	2.192
73	2.232	2.219	2.211	2.207	2.204	2.202	2.200
74	2.238	2.225	2.217	2.214	2.211	2.208	2.207
75	2.243	2.231	2.224	2.220	2.217	2.215	2.213
76	2.249	2.237	2.230	2.226	2.223	2.221	2.220
77	2.255	2.243	2.236	2.232	2.230	2.228	2.226
78	2.261	2.249	2.242	2.239	2.236	2.234	2.233
79	2.267	2.255	2.248	2.245	2.242	2.240	2.239
80	2.272	2.261	2.255	2.251	2.249	2.247	2.245
81	2.277	2.266	2.259	2.256	2.253	2.252	2.250
82	2.282	2.272	2.266	2.262	2.260	2.258	2.257
83	2.287	2.277	2.270	2.267	2.265	2.263	2.262
84	2.291	2.281	2.275	2.272	2.269	2.268	2.266
85	2.297	2.287	2.281	2.278	2.276	2.274	2.273
86	2.301	2.292	2.286	2.283	2.281	2.279	2.278
87	2.305	2.296	2.290	2.287	2.285	2.284	2.282
88	2.310	2.301	2.295	2.292	2.290	2.288	2.287
89	2.314	2.305	2.300	2.297	2.295	2.293	2.292
90	2.318	2.310	2.304	2.302	2.300	2.298	2.297
91	2.323	2.314	2.309	2.306	2.304	2.303	2.302
92	2.327	2.319	2.314	2.311	2.309	2.308	2.307
93	2.331	2.323	2.318	2.316	2.314	2.312	2.311
94	2.334	2.326	2.321	2.319	2.317	2.316	2.315
95	2.339	2.331	2.326	2.324	2.322	2.321	2.320
96	2.341	2.334	2.329	2.327	2.325	2.324	2.323
97	2.346	2.338	2.334	2.332	2.330	2.328	2.328
98	2.349	2.341	2.337	2.335	2.333	2.332	2.331
99	2.353	2.346	2.342	2.339	2.338	2.337	2.336

40 ml sample and 10 ml 0.0100 n acid

S ^o /oo	10	11	12	13	14	15	16
3.00 pH	.881	.875	.867	.861	.858	.853	.851
01	.919	.913	.905	.899	.896	.891	.890
02	.954	.948	.941	.935	.931	.926	.925
03	.990	.984	.977	.971	.968	.963	.962
04	1.024	1.018	1.011	1.005	1.002	.997	.996
05	1.057	1.052	1.045	1.040	1.036	1.032	1.031
06	1.090	1.084	1.078	1.072	1.069	1.065	1.064
07	1.122	1.117	1.110	1.105	1.102	1.098	1.097
08	1.153	1.148	1.142	1.137	1.133	1.129	1.128
09	1.184	1.179	1.173	1.168	1.165	1.161	1.160
10	1.215	1.210	1.204	1.199	1.196	1.192	1.191
11	1.244	1.239	1.233	1.228	1.225	1.222	1.221
12	1.271	1.267	1.261	1.256	1.253	1.249	1.249
13	1.300	1.296	1.290	1.286	1.283	1.279	1.278
14	1.326	1.322	1.316	1.312	1.309	1.305	1.305
15	1.354	1.350	1.344	1.340	1.337	1.334	1.333
16	1.380	1.376	1.370	1.366	1.363	1.360	1.359
17	1.406	1.401	1.396	1.392	1.390	1.386	1.385
18	1.430	1.426	1.421	1.417	1.414	1.411	1.410
19	1.454	1.450	1.445	1.441	1.439	1.436	1.435
20	1.479	1.475	1.470	1.466	1.464	1.460	1.460
21	1.501	1.497	1.493	1.489	1.487	1.483	1.483
22	1.524	1.520	1.516	1.512	1.510	1.506	1.506
23	1.546	1.543	1.538	1.535	1.533	1.530	1.529
24	1.569	1.566	1.561	1.558	1.555	1.553	1.552
25	1.590	1.587	1.583	1.579	1.577	1.574	1.573
26	1.610	1.606	1.602	1.599	1.597	1.594	1.593
27	1.631	1.627	1.623	1.620	1.618	1.615	1.615
28	1.650	1.647	1.643	1.640	1.638	1.635	1.634
29	1.670	1.666	1.662	1.659	1.657	1.655	1.654
30	1.689	1.686	1.682	1.679	1.677	1.675	1.674
31	1.707	1.704	1.700	1.697	1.695	1.693	1.692
32	1.725	1.722	1.718	1.715	1.713	1.711	1.710
33	1.742	1.740	1.736	1.733	1.731	1.729	1.728
34	1.760	1.757	1.754	1.751	1.749	1.747	1.746
35	1.776	1.774	1.770	1.767	1.766	1.764	1.763
36	1.793	1.790	1.787	1.784	1.782	1.780	1.779
37	1.809	1.806	1.803	1.800	1.799	1.796	1.796
38	1.825	1.822	1.819	1.817	1.815	1.813	1.812
39	1.841	1.839	1.836	1.833	1.831	1.829	1.829
40	1.856	1.853	1.850	1.848	1.846	1.844	1.844
41	1.870	1.868	1.865	1.862	1.861	1.859	1.859
42	1.885	1.883	1.880	1.877	1.876	1.874	1.873
43	1.898	1.896	1.893	1.890	1.889	1.887	1.887
44	1.912	1.910	1.907	1.905	1.904	1.902	1.901
45	1.925	1.923	1.920	1.918	1.917	1.915	1.915
46	1.938	1.936	1.933	1.931	1.930	1.928	1.928
47	1.951	1.949	1.947	1.944	1.943	1.941	1.941
48	1.964	1.962	1.960	1.958	1.956	1.955	1.954
49	1.976	1.974	1.971	1.969	1.968	1.966	1.966

40 ml sample and 10 ml 0.0100 n acid

S ^o /oo	10	11	12	13	14	15	16
3.50 pH	1.988	1.986	1.984	1.982	1.981	1.979	1.979
51	2.000	1.998	1.995	1.994	1.992	1.991	1.990
52	2.011	1.009	1.007	1.005	1.004	1.002	2.002
53	2.022	2.021	2.018	2.017	2.015	2.014	2.014
54	2.034	2.032	2.030	2.028	2.027	2.026	2.025
55	2.044	2.042	2.040	2.038	2.037	2.035	2.035
56	2.055	2.053	2.051	2.049	2.048	2.047	2.047
57	2.064	2.063	2.061	2.059	2.058	2.057	2.056
58	2.074	2.073	2.071	2.069	2.068	2.067	2.066
59	2.084	2.082	2.080	2.079	2.078	2.077	2.076
60	2.094	2.092	2.090	2.089	2.088	2.086	2.086
61	2.103	2.102	2.100	2.098	2.098	2.096	2.096
62	2.111	2.110	2.108	2.107	2.106	2.105	2.104
63	2.121	2.120	2.118	2.117	2.116	2.114	2.114
64	2.129	2.128	2.126	2.125	2.124	2.123	2.122
65	2.137	2.136	2.134	2.133	2.132	2.131	2.131
66	2.145	2.144	2.142	2.141	2.140	2.139	2.139
67	2.154	2.152	2.151	2.149	2.149	2.147	2.147
68	2.162	2.160	2.159	2.157	2.157	2.156	2.155
69	2.170	2.169	2.167	2.166	2.165	2.164	2.164
70	2.176	2.175	2.173	2.172	2.171	2.171	2.170
71	2.184	2.183	2.182	2.180	2.180	2.179	2.178
72	2.191	2.190	2.188	2.187	2.186	2.185	2.185
73	2.199	2.198	2.196	2.195	2.194	2.194	2.193
74	2.205	2.204	2.203	2.202	2.201	2.200	2.200
75	2.212	2.211	2.209	2.208	2.208	2.207	2.207
76	2.218	2.217	2.216	2.215	2.214	2.213	2.213
77	2.225	2.224	2.222	2.221	2.221	2.220	2.220
78	2.231	2.230	2.229	2.228	2.227	2.227	2.226
79	2.238	2.237	2.236	2.235	2.234	2.233	2.233
80	2.244	2.243	2.242	2.241	2.240	2.240	2.239
81	2.249	2.248	2.247	2.246	2.245	2.245	2.244
82	2.256	2.255	2.253	2.252	2.252	2.251	2.251
83	2.260	2.260	2.258	2.257	2.257	2.256	2.256
84	2.265	2.264	2.263	2.262	2.262	2.261	2.261
85	2.272	2.271	2.270	2.269	2.268	2.268	2.267
86	2.277	2.276	2.275	2.274	2.273	2.273	2.272
87	2.281	2.281	2.280	2.279	2.278	2.278	2.277
88	2.286	2.286	2.285	2.284	2.283	2.283	2.282
89	2.291	2.290	2.289	2.289	2.288	2.287	2.287
90	2.296	2.295	2.294	2.294	2.293	2.292	2.292
91	2.301	2.300	2.299	2.298	2.298	2.297	2.297
92	2.306	2.305	2.304	2.303	2.303	2.302	2.302
93	2.311	2.310	2.309	2.308	2.308	2.307	2.307
94	2.314	2.313	2.312	2.311	2.311	2.310	2.310
95	2.319	2.318	2.317	2.316	2.316	2.315	2.315
96	2.322	2.321	2.320	2.320	2.319	2.319	2.319
97	2.327	2.326	2.325	2.325	2.324	2.324	2.324
98	2.330	2.329	2.329	2.328	2.327	2.327	2.327
99	2.335	2.334	2.333	2.333	2.332	2.332	2.332

40 ml sample and 10 ml 0.0100 n acid

S°/oo	17	18	19	20-21	22-26	27-29	20-31	32-33
3.00 pH	.846	.844	.843	.840	.837	.840	.843	.844
01	.885	.882	.881	.879	.876	.879	.881	.882
02	.920	.918	.917	.914	.912	.914	.917	.918
03	.957	.955	.954	.952	.949	.952	.954	.955
04	.992	.989	.988	.986	.984	.986	.988	.989
05	1.026	1.024	1.023	1.021	1.018	1.021	1.023	1.024
06	1.059	1.057	1.056	1.054	1.052	1.054	1.056	1.057
07	1.092	1.090	1.089	1.087	1.085	1.087	1.089	1.090
08	1.124	1.122	1.121	1.119	1.117	1.119	1.121	1.122
09	1.156	1.154	1.153	1.151	1.149	1.151	1.153	1.154
10	1.187	1.185	1.184	1.182	1.180	1.182	1.184	1.185
11	1.217	1.215	1.214	1.212	1.210	1.212	1.214	1.215
12	1.245	1.243	1.242	1.240	1.238	1.240	1.242	1.243
13	1.275	1.273	1.272	1.270	1.268	1.270	1.272	1.273
14	1.301	1.299	1.298	1.296	1.295	1.296	1.298	1.299
15	1.329	1.327	1.326	1.325	1.323	1.325	1.326	1.327
16	1.356	1.354	1.353	1.351	1.350	1.351	1.353	1.354
17	1.382	1.380	1.380	1.378	1.376	1.378	1.380	1.380
18	1.407	1.405	1.404	1.403	1.401	1.403	1.404	1.405
19	1.432	1.430	1.429	1.428	1.426	1.428	1.429	1.430
20	1.456	1.455	1.454	1.452	1.451	1.452	1.454	1.455
21	1.480	1.478	1.477	1.476	1.474	1.476	1.477	1.478
22	1.503	1.501	1.500	1.499	1.497	1.499	1.500	1.501
23	1.526	1.524	1.524	1.522	1.521	1.522	1.524	1.524
24	1.549	1.548	1.547	1.545	1.544	1.545	1.547	1.548
25	1.571	1.569	1.568	1.567	1.566	1.567	1.568	1.569
26	1.590	1.589	1.588	1.587	1.586	1.587	1.588	1.589
27	1.612	1.611	1.610	1.609	1.607	1.609	1.610	1.611
28	1.632	1.630	1.630	1.628	1.627	1.628	1.630	1.630
29	1.652	1.650	1.650	1.648	1.647	1.648	1.650	1.650
30	1.671	1.670	1.670	1.668	1.667	1.668	1.670	1.670
31	1.690	1.688	1.688	1.687	1.685	1.687	1.688	1.688
32	1.708	1.707	1.706	1.705	1.704	1.705	1.706	1.707
33	1.726	1.725	1.724	1.723	1.722	1.723	1.724	1.725
34	1.744	1.743	1.742	1.741	1.740	1.741	1.742	1.743
35	1.761	1.760	1.759	1.758	1.757	1.758	1.759	1.760
36	1.777	1.776	1.776	1.775	1.773	1.775	1.776	1.776
37	1.794	1.793	1.792	1.791	1.790	1.791	1.792	1.793
38	1.810	1.809	1.809	1.808	1.807	1.808	1.809	1.809
39	1.827	1.826	1.825	1.824	1.823	1.824	1.825	1.826
40	1.842	1.841	1.840	1.839	1.838	1.839	1.840	1.841
41	1.857	1.856	1.855	1.854	1.853	1.854	1.855	1.856
42	1.872	1.871	1.870	1.869	1.868	1.869	1.870	1.871
43	1.885	1.884	1.883	1.882	1.882	1.882	1.883	1.884
44	1.900	1.899	1.898	1.897	1.896	1.897	1.898	1.899
45	1.913	1.912	1.912	1.911	1.910	1.911	1.912	1.912
46	1.926	1.925	1.925	1.924	1.923	1.924	1.925	1.925
47	1.939	1.938	1.938	1.937	1.936	1.937	1.938	1.938
48	1.953	1.952	1.951	1.950	1.950	1.950	1.951	1.952
49	1.964	1.963	1.963	1.962	1.961	1.962	1.963	1.963

40 ml sample and 10 ml 0.0100 n acid

S°/oo	17	18	19	20-21	22-26	27-29	30-31	32-33
3.50 pH	1.977	1.977	1.976	1.975	1.975	1.975	1.976	1.977
51	1.989	1.988	1.988	1.987	1.986	1.987	1.988	1.988
52	2.001	2.000	1.999	1.999	1.998	1.999	1.999	2.000
53	2.012	2.011	2.011	2.010	2.009	2.010	2.011	2.011
54	2.024	2.023	2.023	2.022	2.021	2.022	2.023	2.023
55	2.034	2.033	2.033	2.032	2.031	2.032	2.033	2.033
56	2.045	2.044	2.044	2.043	2.043	2.043	2.044	2.044
57	2.055	2.054	2.054	2.053	2.053	2.053	2.054	2.054
58	2.065	2.064	2.064	2.063	2.063	2.063	2.064	2.064
59	2.075	2.074	2.074	2.073	2.073	2.073	2.074	2.074
60	2.085	2.084	2.084	2.083	2.083	2.083	2.084	2.084
61	2.095	2.094	2.094	2.093	2.093	2.093	2.094	2.094
62	2.103	2.102	2.102	2.102	2.101	2.102	2.102	2.102
63	2.113	2.112	2.112	2.112	2.111	2.112	2.112	2.112
64	2.121	2.121	2.120	2.120	2.119	2.120	2.120	2.121
65	2.130	2.129	2.129	2.128	2.128	2.128	2.129	2.129
66	2.138	2.137	2.137	2.136	2.136	2.136	2.137	2.137
67	2.146	2.146	2.145	2.145	2.144	2.145	2.145	2.146
68	2.154	2.154	2.154	2.153	2.152	2.153	2.154	2.154
69	2.163	2.162	2.162	2.161	2.161	2.161	2.162	2.162
70	2.169	2.169	2.169	2.168	2.168	2.168	2.169	2.169
71	2.177	2.177	2.177	2.176	2.176	2.176	2.177	2.177
72	2.184	2.184	2.183	2.183	2.182	2.183	2.183	2.184
73	2.192	2.192	2.192	2.191	2.191	2.191	2.192	2.192
74	2.199	2.199	2.198	2.198	2.197	2.198	2.198	2.199
75	2.206	2.205	2.205	2.205	2.204	2.205	2.205	2.205
76	2.212	2.212	2.212	2.211	2.211	2.211	2.212	2.212
77	2.219	2.218	2.218	2.218	2.217	2.218	2.218	2.218
78	2.225	2.225	2.225	2.224	2.224	2.224	2.225	2.225
79	2.232	2.232	2.231	2.231	2.231	2.231	2.231	2.232
80	2.239	2.238	2.238	2.238	2.237	2.238	2.238	2.238
81	2.244	2.243	2.243	2.243	2.242	2.243	2.243	2.243
82	2.250	2.250	2.250	2.249	2.249	2.249	2.250	2.250
83	2.255	2.255	2.255	2.254	2.254	2.254	2.255	2.255
84	2.260	2.260	2.260	2.259	2.259	2.259	2.260	2.260
85	2.267	2.266	2.266	2.266	2.266	2.266	2.266	2.266
86	2.272	2.271	2.271	2.271	2.271	2.271	2.271	2.271
87	2.277	2.276	2.276	2.276	2.275	2.276	2.276	2.276
88	2.282	2.281	2.281	2.281	2.281	2.281	2.281	2.281
89	2.287	2.286	2.286	2.286	2.285	2.286	2.286	2.286
90	2.292	2.291	2.291	2.291	2.291	2.291	2.291	2.291
91	2.297	2.296	2.296	2.296	2.295	2.296	2.296	2.296
92	2.302	2.301	2.301	2.301	2.300	2.301	2.301	2.301
93	2.306	2.306	2.306	2.306	2.305	2.306	2.306	2.306
94	2.310	2.309	2.309	2.309	2.309	2.309	2.309	2.309
95	2.315	2.314	2.314	2.314	2.314	2.314	2.314	2.314
96	2.318	2.318	2.318	2.317	2.317	2.317	2.318	2.318
97	2.323	2.323	2.323	2.322	2.322	2.322	2.323	2.323
98	2.326	2.326	2.326	2.326	2.325	2.326	2.326	2.326
99	2.331	2.331	2.331	2.331	2.330	2.331	2.331	2.331

50 ml sample and 15 ml 0.0100 n acid

S ^o /oo	33	34	35	36	37	38	39	40
3.00 pH	1.278	1.280	1.283	1.285	1.287	1.289	1.292	1.292
01	1.317	1.320	1.322	1.325	1.326	1.329	1.331	1.331
02	1.354	1.357	1.359	1.362	1.363	1.366	1.368	1.368
03	1.393	1.395	1.398	1.400	1.401	1.404	1.406	1.406
04	1.429	1.431	1.433	1.436	1.437	1.439	1.442	1.442
05	1.466	1.468	1.470	1.473	1.474	1.476	1.478	1.478
06	1.500	1.502	1.505	1.507	1.508	1.510	1.513	1.513
07	1.535	1.537	1.539	1.541	1.542	1.545	1.547	1.547
08	1.566	1.569	1.571	1.573	1.574	1.576	1.578	1.578
09	1.599	1.602	1.604	1.606	1.607	1.609	1.611	1.611
10	1.633	1.635	1.637	1.639	1.640	1.642	1.644	1.644
11	1.663	1.665	1.667	1.669	1.670	1.672	1.674	1.674
12	1.692	1.694	1.696	1.698	1.699	1.701	1.703	1.703
13	1.724	1.726	1.728	1.730	1.731	1.733	1.735	1.735
14	1.751	1.752	1.754	1.756	1.757	1.759	1.761	1.761
15	1.780	1.782	1.783	1.785	1.786	1.788	1.790	1.790
16	1.807	1.809	1.811	1.813	1.814	1.816	1.817	1.817
17	1.835	1.837	1.839	1.841	1.841	1.843	1.845	1.845
18	1.862	1.864	1.865	1.867	1.868	1.870	1.871	1.871
19	1.887	1.889	1.890	1.892	1.893	1.895	1.896	1.896
20	1.914	1.915	1.917	1.918	1.919	1.921	1.923	1.923
21	1.937	1.939	1.941	1.942	1.943	1.945	1.946	1.946
22	1.961	1.963	1.964	1.966	1.967	1.968	1.970	1.970
23	1.985	1.987	1.988	1.990	1.990	1.992	1.993	1.993
24	2.009	2.010	2.012	2.013	2.014	2.016	2.017	2.017
25	2.031	2.033	2.034	2.036	2.037	2.038	2.039	2.039
26	2.053	2.054	2.055	2.057	2.058	2.059	2.060	2.060
27	2.075	2.077	2.078	2.079	2.080	2.081	2.083	2.083
28	2.095	2.096	2.098	2.099	2.100	2.101	2.103	2.103
29	2.116	2.118	2.119	2.120	2.121	2.122	2.124	2.124
30	2.137	2.139	2.140	2.141	2.142	2.143	2.145	2.145
31	2.156	2.157	2.159	2.160	2.160	2.162	2.163	2.163
32	2.175	2.176	2.177	2.178	2.179	2.180	2.181	2.181
33	2.194	2.196	2.197	2.198	2.199	2.200	2.201	2.201
34	2.213	2.214	2.215	2.217	2.217	2.218	2.219	2.219
35	2.230	2.231	2.232	2.234	2.234	2.235	2.237	2.237
36	2.247	2.249	2.250	2.251	2.251	2.253	2.254	2.254
37	2.265	2.266	2.267	2.268	2.269	2.270	2.271	2.271
38	2.282	2.283	2.284	2.285	2.286	2.287	2.288	2.288
39	2.299	2.300	2.301	2.302	2.303	2.304	2.305	2.305
40	2.315	2.316	2.317	2.318	2.319	2.320	2.321	2.321
41	2.330	2.331	2.332	2.333	2.333	2.334	2.335	2.335
42	2.345	2.346	2.347	2.348	2.349	2.349	2.351	2.351
43	2.359	2.369	2.361	2.362	2.362	2.363	2.364	2.364
44	2.375	2.376	2.376	2.376	2.378	2.379	2.380	2.380
45	2.388	2.389	2.390	2.391	2.391	2.392	2.393	2.393
46	2.402	2.403	2.404	2.405	2.406	2.406	2.407	2.407
47	2.416	2.417	2.417	2.418	2.419	2.420	2.421	2.421
48	2.430	2.431	2.432	2.433	2.433	2.434	2.435	2.435
49	2.442	2.443	2.444	2.445	2.445	2.446	2.447	2.447

50 ml sample and 15 ml 0.0100 n acid

S ^o /oo	33	34	35	36	37	38	39	40
3.50 pH	2.455	2.456	2.457	2.458	2.458	2.459	2.460	2.460
51	2.467	2.468	2.469	2.470	2.470	2.471	2.472	2.472
52	2.479	2.480	2.481	2.482	2.482	2.483	2.484	2.484
53	2.491	2.492	2.493	2.494	2.494	2.495	2.495	2.495
54	2.504	2.505	2.506	2.507	2.507	2.508	2.509	2.509
55	2.514	2.514	2.515	2.516	2.516	2.517	2.518	2.518
56	2.526	2.526	2.527	2.528	2.528	2.529	2.530	2.530
57	2.536	2.537	2.538	2.538	2.539	2.539	2.540	2.540
58	2.547	2.548	2.548	2.549	2.549	2.550	2.551	2.551
59	2.557	2.558	2.559	2.559	2.560	2.560	2.561	2.561
60	2.568	2.569	2.569	2.570	2.570	2.571	2.572	2.572
61	2.577	2.578	2.579	2.579	2.580	2.580	2.581	2.581
62	2.587	2.587	2.588	2.588	2.589	2.589	2.590	2.590
63	2.597	2.598	2.598	2.599	2.599	2.600	2.601	2.601
64	2.605	2.606	2.606	2.607	2.607	2.608	2.608	2.608
65	2.614	2.615	2.616	2.616	2.616	2.617	2.618	2.618
66	2.622	2.623	2.624	2.624	2.624	2.625	2.626	2.626
67	2.632	2.632	2.633	2.633	2.634	2.634	2.635	2.635
68	2.640	2.640	2.641	2.641	2.642	2.642	2.643	2.643
69	2.649	2.649	2.650	2.650	2.651	2.651	2.652	2.652
70	2.655	2.656	2.657	2.657	2.657	2.658	2.658	2.658
71	2.663	2.664	2.664	2.665	2.665	2.666	2.666	2.666
72	2.671	2.672	2.672	2.673	2.673	2.674	2.674	2.674
73	2.679	2.680	2.680	2.681	2.681	2.682	2.682	2.682
74	2.686	2.686	2.687	2.687	2.688	2.688	2.689	2.689
75	2.694	2.694	2.695	2.695	2.696	2.696	2.696	2.696
76	2.701	2.701	2.701	2.702	2.702	2.703	2.703	2.703
77	2.707	2.708	2.708	2.709	2.709	2.709	2.710	2.710
78	2.714	2.714	2.715	2.715	2.715	2.716	2.716	2.716
79	2.720	2.721	2.721	2.722	2.722	2.722	2.723	2.723
80	2.728	2.729	2.729	2.730	2.730	2.730	2.731	2.731
81	2.732	2.733	2.733	2.734	2.734	2.734	2.735	2.735
82	2.740	2.741	2.741	2.741	2.742	2.742	2.742	2.742
83	2.746	2.746	2.746	2.747	2.747	2.747	2.748	2.748
84	2.750	2.750	2.750	2.751	2.751	2.751	2.752	2.752
85	2.758	2.758	2.758	2.759	2.759	2.759	2.760	2.760
86	2.763	2.763	2.764	2.764	2.764	2.764	2.765	2.765
87	2.767	2.767	2.768	2.768	2.768	2.768	2.769	2.769
88	2.772	2.772	2.773	2.773	2.773	2.774	2.774	2.774
89	2.777	2.778	2.778	2.778	2.779	2.779	2.779	2.779
90	2.783	2.783	2.783	2.784	2.784	2.784	2.785	2.785
91	2.788	2.788	2.789	2.789	2.789	2.789	2.790	2.790
92	2.793	2.794	2.794	2.794	2.794	2.795	2.795	2.795
93	2.799	2.799	2.799	2.800	2.800	2.800	2.800	2.800
94	2.801	2.802	2.802	2.802	2.802	2.803	2.803	2.803
95	2.807	2.807	2.807	2.807	2.808	2.808	2.808	2.808
96	2.811	2.811	2.811	2.811	2.812	2.812	2.812	2.812
97	2.816	2.816	2.816	2.817	2.817	2.817	2.817	2.817
98	2.818	2.819	2.819	2.819	2.819	2.820	2.820	2.820
99	2.824	2.824	2.824	2.825	2.825	2.825	2.825	2.825

Standardization of Hydrochloric Acid Solutions
to be used in the Determination of Alkalinity

by

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The experiences from two intercalibrations of alkalinity show, that the hydrochloric acid solutions used must be standardized very carefully. It is recommended to use two standard substances, viz. borax and potassium iodate. The latter is used with high accuracy for standardization of the thiosulphate solutions in the determination of oxygen according to Winkler.

First, dilute concentrated analytical grade or fixanal HCl solution to approx. proper normality, and then determine the exact titre as follows.

Borax, rational equivalent weight 190.607, is an excellent standard substance and the standardization can be done without any titration error if methyl red is employed as indicator. A reference solution is used with just as much boric acid, sodium chloride and indicator, as the titrated solution contains at the equivalence point.

Analytical grade borax is recrystallized below 50°C and dried first in air and then to constant weight in a desiccator over lightly moist sodium bromide. Stock reference solution is 0.1 M boric acid solution containing 0.05 M sodium chloride. The weighted amount of borax in mg times 0.105 gives the number of ml stock reference solution needed for the reference working solution.

Potassium iodate. Acids may be determined iodometrically by utilizing the reaction $IO_3^- + 5 I^- + 6 H^+ \rightarrow 3 I_2 + 3 H_2O$. The acid solution is treated with an excess of neutral iodide and iodate and liberated iodine titrated with standard thiosulphate solution.

Dissolve in a clear 100 ml conical flask with a glass stopper approx. 150 mg of analytical grade KIO_3 in 20 ml of dist. water. Dissolve in this solution ca. 1 g of analytical grade NaI, and add immediately with a calibrated pipette 10 ml of the HCl solution to be standardized. After standing for 5 minutes the liberated iodine is titrated with standard thiosulphate solution with starch as indicator.

A blank is made as described above, with 10 ml of dist. water instead of the HCl solution. According to the author's experiences, a neutral mixture of iodate and sodium iodide remains colorless for a longer period, than an iodate solution containing potassium iodide.

Notes on Analytical Methods and Problems

by

R. Johnston

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1. Analysis of nitrogen compounds

1.11 Nitrate (manual). Hydrazine reduction.

The preferred method employs the reduction by hydrazine (Mullin and Riley, 1955) followed by diazotisation and dye formation as described by Strickland and Parsons (1960).

The method is quite satisfactory though laborious, as it requires calibration on each occasion since the efficiency of the reduction varies from batch to batch. Since presence and access of air can be an important factor, a uniform set of glass-stoppered bottles is needed and all operations prior to colour development should be carried out according to a tight time schedule. Supplies of N-1-naphthyl-ethylene diamine dihydrochloride have been found to vary in quality and indeed one batch was returned as impure.

It has been found that the addition of acetone laid down in most methods of this type is unnecessary and may be omitted.

1.12 Nitrate (manual). Cadmium reduction (Morris and Riley, 1963).

Our experience with cadmium reductor columns brought no consistent success. Columns varied in their efficiencies and no reproducible procedure could be established (see next section).

1.13 Nitrate (automated). Cadmium reduction.

The cadmium reductor method of Brewer and Riley (1965) is capable of more reproducible results than the manual method. However it was found that reduction depended on the amount of air present and ceased if nitrogen segmentation was substituted for air segmentation, which led to doubts concerning the effects of (a) the varying oxygen contents of the sea-water samples (b) changes in the condition of the column following prolonged sequences of low or high nitrate samples.

1.14 Nitrate (automated). Copper-cadmium reduction.

The copper-cadmium reductor of Armstrong and La Fond (1966) takes care to eliminate air segmentation before the reduction stage and thus avoids the objections raised in the previous method. The use of packed columns is not a desirable practice as they introduce considerable carry-over between samples. Better results might ensue if capillary cadmium tubing could be obtained, but a search in U.K.

markets was unfruitful. One should note carefully that the 0.1 Molar tetrasodium EDTA stock solution is used at a specified working strength of 0.02 Normal, i.e. 20 times dilution; this weak reagent prolongs the life of the reductor.

1.15 Nitrate (manual). Nitration methods.

In an attempt to circumvent nitrate estimation via some form of reduction to nitrite (or ammonia), almost all known methods have been tried in which nitrate is used in the nitration of a sensitive organic compound. In no case was nitration effective at a suitably low concentration in sea water.

1.2 Nitrite (cf. Strickland and Parsons, 1960).

No difficulties have been encountered in the determination of nitrite by either the manual or the automated methods of analysis.

1.31 Ammonia (manual).

The method described in last year's contribution (Johnston, 1966) has been used with success. There is difficulty in preparing the solution of 3-methyl-1-phenylpyrazol-5-one required for the "mono" reagent. A solution in 50% ethanol is better. It speeds up the reaction with Pyrazolone Blue, improves the carbon tetrachloride separation and extends the range of rubazoic acid which can be efficiently extracted in one operation. This modified reagent is therefore recommended.

1.32 Ammonia (automated).

The above method is in the process of development for Auto Analysis and it is hoped to report on progress at the 1967 ICES meetings.

1.4 Particulate nitrogen (manual, semi-automated).

Total nitrogen (5 to 500 µg) is determined on particulate matter by Kjeldahl digestion followed by the usual hypochlorite-sodium phenate colour reaction. The digestion is performed manually followed by either (i) micro-Kjeldahl distillation, (ii) Leurquin transfer and manual colorimetry or (iii) automatic analysis directly on the digested sample suitably diluted. The methods are at present being compared for efficiency and ease of operation.

2. Sampling techniques and samplers

Most chemical samples are taken with the Pettersson-Nansen insulated water bottle or the Nansen reversing water bottle. Plastic sampling devices (up to 10 l.) are occasionally used.

3. Oxygen saturation and related problems

3.1 Winkler oxygen determination.

Little trouble is experienced with (unmodified) Winkler oxygen determinations in open sea water. In estuaries and polluted coastal waters, however, a proportion of the most polluted samples, as indexed by B.O.D. and other parameters, show unduly high oxygen values. This means that certain interfering oxidising substances are present. Interferences (reducing substances) producing markedly low oxygen values are less unexpected. This experience has been corroborated by inspectors of various river purification boards working on fresh and brackish water samples. It would be interesting to know if others present have had this experience.

The background to this problem appears to offer a challenge to physical chemists and biochemists. The basic Winkler technique involves the oxidation of manganous hydroxide in moderately alkaline medium. There are many modifications of the Winkler method (Rideal-Stewart, Theriault, Alsterberg, Ohle, phosphoric acid, sulfamic acid and others) to cope with various interfering substances. All these interfering substances are active oxygen donors or acceptors which modify the oxidation-reduction potential of the solution. The respiratory pigments of marine animals must compete with these for oxygen. In water receiving pulp mill wastes, nitrites, or heavy organic loading, it has been shown that the Winkler method, the oxygen electrode method and the modified Winkler methods may all yield results significantly differing from one another. Often, the oxygen content of natural waters is a useful guide to its quality for marine life. Which method determines most closely oxygen available to respiratory pigments. How may oxygen content, oxidation reduction potential and respiration be related to one another under the non-ideal conditions of polluted waters?

I might mention at this point, the need for simple and rapid techniques for the measurement of dissolved oxygen in interstitial water in situ or in separated samples.

3.2 Permanganate value (Appendix 1).

A note on this determination is appended which may prove of interest to marine chemists working on pollution problems.

3.3 Methylene Blue factor (Appendix 2).

It is occasionally of value to have a measure of the rate of change of a sea-water sample towards anaerobic conditions. A note on an ad hoc procedure is appended which also is of main interest to marine chemists faced with pollution problems.

4. Determination of alkalinity, and calibration of acids and bases

Nothing to contribute.

5. Wanted information

5.1 User experience is requested comparing the various manual and automated silicate methods.

5.2 There is a considerable need for nutrient and oxygen analyses of interstitial water collected underwater by divers or automatically or from sands and muds within the tidal range on beaches. Advice is sought from anyone having such equipment and/or analytical experience.

5.3 Has anyone experience with stationary or polarographic electrode systems for oxygen in the bottom interstitial environment - also apparatus for in situ interstitial measurement of salinity. The pCl electrode or a similar device would appear to be suitable for the salinity application but is not yet commercially available.

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APPENDIX 1

Method: Permanganate Value (P.V. 27° C in Sea Water

Modifications

Main alteration is use of phosphoric acid in place of H₂SO₄ to suppress effects of chloride and any iron present.

Procedure

Place 250 ml sea-water sample in 500 ml glass-stoppered conical flask or bottle; add 50 ml of solution N/80 KMnO₄ and 10 ml dilute phosphoric acid and mix. Place flask in waterbath at 27° C for four hours. Remove from bath, add 5 ml KI solution and titrate liberated iodine with N/50 sodium thiosulphate. For "blank", run replicates using glass distilled water (or if reagents are satisfactory, titrate D.W. sample without standing four hours at 27°C).

Calculation

$$\begin{aligned} \text{Permanganate value (P.V. } 27^{\circ}\text{C)} &= \frac{(\text{Blank-titre}) \times 100}{\text{volume of sample (ml)}} \times \text{factor to} \\ & \hspace{15em} \text{bring thio to N/80} \\ &= \text{p.p.m.} \end{aligned}$$

Results

Clean sea-water 0.1 - 0.3 p.p.m.

Polluted sea-water up to 10 p.p.m. has been found.

Reagents

- (i) N/80 Potassium permanganate prepared from stabilised N/1 solution.
- (ii) Dilute phosphoric acid; 100 ml orthophosphoric acid + 300 ml glass distilled water.
- (iii) Potassium iodide 10 g/100 ml. distilled water.

Sources

- Klein, L. 1959. "River Pollution". 1. Chemical Analysis", London, Butterworths, 206 pp.
- Roberts, R.F. 1955. "Oxygen absorbed from acid permanganate in the presence of chloride." Analyst, 80, 517-519.
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APPENDIX 2

Method: Methylene Blue Factor (Tentative)

Modification

Sea water samples were found never to fail the usual Methylene Blue stability test* but some indication of the rate of progress towards anaerobic conditions was required. For this, the fading of a weak solution of Methylene Blue over a period of five days at 20°C was used. Results were expressed as percentage of the blank in glass distilled water.

Reagents

0.100 g methylene blue dye dissolved and made up to 500 ml in fresh glass distilled water.

Method

Add exactly 1.00 ml Methylene Blue solution to the sample which completely fills a 5 oz. (150 ml) glass stoppered bottle. Insert stopper and keep dark for five days at room temperature or constant temperature room (15°C) if available. Run replicates using glass distilled water for "blank" determinations.

Measure with colorimeter using red or deep red filters and 2 cm cell.

Calculation

The volume of each bottle must be known and duplicates (initial and final) are necessary if the water is turbid or coloured.

- (1) adjust O.D. reading of samples and blanks by factor

$$\text{Corr. O.D.} = \frac{100}{\text{volume}} \times \text{O.D. observed}$$

$$(2) \frac{\text{blank O.D.}_{\text{Corr}} - \text{sample O.D.}_{\text{Corr}}}{\text{blank O.D.}_{\text{Corr}}} \times 100$$

= % Methylene Blue Factor

Results

Values vary considerably in polluted waters, not necessarily in direct proportion to Permanganate Value or B.O.D. Results down to 58% colour remaining have been recorded; clean sea water gives values of 75% and above.

* Ministry of Housing and Local Government. 1956. "Methods of chemical analysis as applied to sewage and sewage-effluents." 2nd Ed. H.M.S.O., London, 96 pp.