THE DETERMINATION AND

OCCURRENCE OF ALUMINUM

IN SEA WATER

by

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ABSTRACT

A method was developed for the determination of aluminum in sea water using oxine as a reagent.

Extraction of aluminum oxinate by chloroform from acidic solution was impeded by the presence of fluoride in sea water. The fluoride interference was less severe in basic solution and it was possible to extract aluminum oxinate from sea water at a pH of 8 with no loss of sensitivity due to the presence of fluoride. Iron and copper were complexed with cyanide in reducing solution and manganese oxinate was removed by extracting it from the chloroform into an aqueous acidic solution. Other interfering ions in sea water were present in amounts too small to be significant. The absorbancy of the aluminum oxinate complex was measured at 395 mμ and compared with a calibration curve. The aluminum concentration in sea water ranged from 2 - 42 μg./l. Values for coastal water were higher than for oceanic water.

ACKNOWLEDGEMENT

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INTRODUCTION

Trace Constituents

Aluminum is believed to occur in such small amounts in sea water that it is classed as a trace constituent. The concentrations of various ions in sea water are listed in Table I (10).

Table I

The composition of sea water (10)

Ion	Concentration mg. / l.	Ion	Concentration mg. / l.
Aluminum	0-1.9	Lithium	0.1
Antimony	0.0002	Magnesium	1330
Arsenic	0.001-0.005	Manganese	0.001-0.01
Barium	0.03-0.09	Mercury	0.00003
Borate	26	Molybdenum	0.0003-0.016
Bismuth	0.0002	Nickel	0.00001-0.006
Bromide	66	Nitrate	0.001-0.6
Cadmium	0.000032-0.000057	Phosphate	0.001-0.06
Cesium	0.002	Potassium	390
Calcium	420	Radium	$0.7-5.8 \times 10^{-10}$
Carbon	1-2.5	Rubidium	0.2
Cerium	0.0004	Scandium	0.00004
Chloride	19800	Selenium	0.004
Chromium	0.001-0.0025	Silicate	1-3
Cobalt	0.0001	Silver	0.00015-0.0003
Copper	0.001-0.025	Sodium	11100
Deuterium	16	Strontium	10
Fluoride	1.4	Sulfate	2760
Gallium	0.0005	Thorium	$10^{-5}-10^{-6}$
Germanium	identified	Tin	0.003
Gold	$4-6 \times 10^{-6}$	Titanium	0.001-0.009
Iodide	0.05	Vanadium	0.0002-0.007
Iron	0.001-0.010	Yttrium	0.0003
Lanthanum	0.0003	Zinc	0.008-0.014
Lead	0.004		

According to Sandell (20), a macro constituent is one that occurs in concentration greater than 0.01%, and a micro or trace constituent occurs in concentration less than 0.01%. Gravimetric and volumetric techniques are not generally applicable to trace determinations but rather colorimetric and spectrographic methods are employed. These can be applied to concentrations as low as 10^{-5}%. This lower limit can be further reduced by means of concentration techniques such as extraction, precipitation or distillation.

Colorimetry

A colorimetric method depends on the formation of a colored solution with color intensity proportional to the concentration of the constituent to be determined. The color intensity can be estimated visually or by means of a photometer. The Beer-Lambert law (20), which relates light absorption to concentration and thickness of the colored sample is written as follows

$$\frac{I_t}{I_o} = e^{-kcl}$$

where I_t = transmitted light intensity.

I_o = incident intensity.

k = molar absorptivity.

c = concentration in moles / l.

l = thickness of sample in cm.

If the photometer reads in log $\frac{I_o}{I_t}$ or absorbancy, a plot of

concentration against absorbancy should give a straight line
if Beer's law applies. The usual photometric method is to
vary the concentration and hold the sample thickness constant.
If the photometer supplies monochromatic radiant energy,
absorption should be studied at a wavelength of maximum
absorption. This provides maximum sensitivity and reduces
the effect of interfering substances that have absorption
peaks different from that of the trace being determined.

Several components of a mixture may react in the
same way with a particular colorimetric reagent to form
compounds with absorption peaks at nearly the same wave-
length. In such a mixture all the interfering components
must be removed or otherwise prevented from reacting with
the reagent. This may be done by pH control in extraction,
by electrolysis, distillation, or complex formation.

The absorption of the unknown is compared with a
blank which should differ from the unknown in composition
only by lacking the component being determined.

Determination of Aluminum

Several colorimetric reagents have been proposed
for the determination of traces of aluminum. The classical
reagent is aluminon, which was first used in 1925 (9,30).
Other colorimetric reagents are alizarin red S (1),

hematoxylin (11), quercetin (4), and quinalizarin (16).
Reagents giving fluorescence reactions with aluminum are
Pontachrome Blue Black R (28), and morin (29). The reagent
8-quinolinol (oxine) can be applied to either colorimetric
or fluorimetric methods (2, 25).

The first mention of aluminum in sea water was
made by Forchhammer (5) who reported that "aluminum is
easily detectable in sea water ". Unpublished work by
Thompson and Robinson (cited in (24)) indicated that the
aluminum concentration was 600-2400 µg./l. The estimations
were made with aluminon but no effort was made to eliminate
contamination from glass sample bottles. Determinations
near the San Juan Archipelago indicated that the aluminum
concentration was directly related to the volume of river
run-off.

In 1939 Haendler and Thompson (8), suggested
oxine as the most suitable reagent for the estimation of
aluminum in sea water. They used an indirect method which
involved the precipitation of aluminum oxinate. The collected
precipitate was then dissolved and coupled with diazotized
sulfanilic acid (27), and the intensity of the colored
compound was compared with standards. They reported values
of 160-1800 µg./l., with the high values occurring in the
spring.

Ishibashi and Kawai (14) used aluminon to estimate
the aluminum concentration in sea water off the Japanese

coast. They could not establish vertical distributions since the concentrations found varied only from 295-325 µg./l.

Simons, Monaghan and Taggart (22) determined aluminum in Atlantic coastal water by means of the fluorescence reagent, Pontachrome Blue Black R. They reported values of 0-7 µg. A 1/l. with an average of 2.5 µg. / l.

Oxine as a Reagent for Aluminum

The reagent chosen for the aluminum determinations reported here was oxine. Aluminum oxinate can be extracted by chloroform from either acidic or basic aqueous solutions (7,18).

By proper control of pH and other conditions it should be possible to make this procedure quite specific for aluminum, although oxine can react with many metals. The absorbancy of the chloroform solution can be measured at the absorption peak of 395 mµ. (18) or the fluorescence can be measured with a fluorimeter (25).

Aluminum oxinate is slightly soluble in water (21). Moeller (18) has reported that aluminum oxinate can be extracted with difficulty by chloroform from a solution at pH 4.3-4.6. Gentry and Sherrington (7) claimed complete extraction with 1/2% oxine in chloroform in the pH range 4.5-11.5. If the solution was made nearly neutral (pH 6.5-8) before the addition of oxine the extraction was incomplete, possibly because of the formation of aluminum hydroxide.

They also listed the many interfering ions. Metallic ions reacting at both pH5 and pH9 were Al, Sb, Bi, Cd, Ce IV, Co, Cu, Fe, Pb, Hg, Ni, Sn II, Ti, U, and Zn. Those reacting at pH 9 but not at pH 5 were Be, Ce III, Mg, Mn, Nd, and Pr. Magnesium oxinate forms a dihydrate on shaking and dissolves in the water layer. Anions that interfere by preventing extraction of the aluminum oxinate include fluoride, which interferes badly in both acidic and basic solution, and tartrate and phosphate which interfere only slightly. They found it possible to complex Cu, Ni, Co, Zn and Cd in basic solution with potassium cyanide and to complex Fe in basic solution under reducing conditions with potassium cyanide.

Lacroix (17) did extensive work on the equilibrium of aluminum oxinate between water and chloroform. He reported the solubilities listed in Table II.

Tullo, Stringer and Harrison (25) applied the fluorescence of aluminum oxinate in chloroform to the determination of aluminum in beer. In this method they were able to eliminate the effect of interfering ions to a large extent since only Al, Cd, Zn and Be gave fluorescent oxinates. They reported a sensitivity of 10 ug. Al/l.

The removal of interferences in the oxine method may also be effected by pH control (19), by electrolysis with a mercury cathode (15), or by complex formation and extraction (3, 12, 13).

Table II

Solubility of Aluminum Oxinate (17)

	Solubility @ 18°C	
	chloroform	water
oxine	2.55M	3.56×10^{-3} M
Al oxinate	4.5×10^{-2}M	$K_{sp} = 10^{-32.3}$

The calculated value of the equilibrium constant for aluminum oxinate between equal volumes of water and chloroform was

$$\frac{\left[Al^{+++}\right]\left[Ox^{-}\right]^{3}}{\left[Al(Ox)_{3}\right]_{CHCl_{3}}} = 10^{-31.1}$$

EXPERIMENTAL

Apparatus and Materials

- All absorbancy readings were made with a Beckman Model DU Spectrophotometer with photomultiplier attachment.
- All pH readings were made on a Beckman Model G pH Meter.
- Distilled water was obtained by distillation from alkaline permanganate in a tin-lined still.
- Ammonium hydroxide was prepared by distilling reagent grade ammonium hydroxide and dissolving the liberated ammonia in distilled water.
- All chemicals were reagent grade or better unless otherwise specified.
- Acetate buffer was prepared by dissolving 18.7 gm. ammonium acetate and 30 ml. glacial acetic acid in distilled water and diluting to 100 ml. One ml. of this made the pH 4.3-4.6 in a 250 ml. sample.
- Ammonia buffer was prepared by dissolving 71 gm. ammonium nitrate in distilled water and diluting with water and ammonia to make the final solution 0.5M in ammonia. One ml. of this made the pH 7.8-8.2 in a 250 ml. sample.
- Natural sea water from Departure Bay, B.C. was collected and stored in a glass carboy. Sea water samples were taken on a North Pacific cruise and were stored in glass bottles. Inlet water was collected on a coastal cruise and was stored in polyethylene bottles.
- Synthetic sea water was prepared by the method of Lyman and Fleming (23, p.186). The composition is given in Table III.

Table III

Synthetic sea water (23)

Reagent	Concentration
NaCl	23.476
$MgCl_2$	4.981
Na_2SO_4	3.917
$CaCl_2$	1.102
KCl	0.664
$NaHCO_3$	0.192
KBr	0.096
H_3BO_3	0.026
$SrCl_2$	0.024
NaF (C.P.)	0.003

The above salts were dissolved
in distilled water and diluted
to one litre.

Procedure

The method described here, using oxine, is at least as sensitive as any other method available.

Samples of 250 ml. volume were extracted in pyrex separatory funnels with chloroform solutions of oxine. The absorbancies of the chloroform extracts were read against pure chloroform in one cm. cells at 395 mμ using the spectrophotometer. The extractions were done from both acidic and basic solution. The effects of shaking time, oxine concentration, pH, and interference by various ions were studied.

RESULTS

Acidic Solution

In all of the following procedures aqueous samples
of 250 ml. volume were kept at a pH 4.3-4.6 during extraction
by means of the acetate buffer which made the final solution
0.01M in ammonium acetate and 0.02M in acetic acid.

Absorption Spectra

The absorption spectrum of aluminum 8-quinolinate
(oxinate) was obtained by extracting distilled water contain-
ing 100 μg.Al/l. (as potassium aluminum sulfate) with two
5 ml. portions of 5% oxine in chloroform for one minute each.
The combined extracts were diluted to 10 ml. and compared
against chloroform at various wavelengths. Distilled water
alone was treated as above to obtain corrections for
absorption by oxine alone. The results are shown in Figure 1.
The broad absorption band of aluminum oxinate from 380-400 mμ
is shown clearly.

An experiment showed that no more aluminum was
removed from distilled water in three extractions than in
two extractions with 5% oxine.

Fig. 1
Absorption spectra of oxine and aluminum oxinate
in chloroform
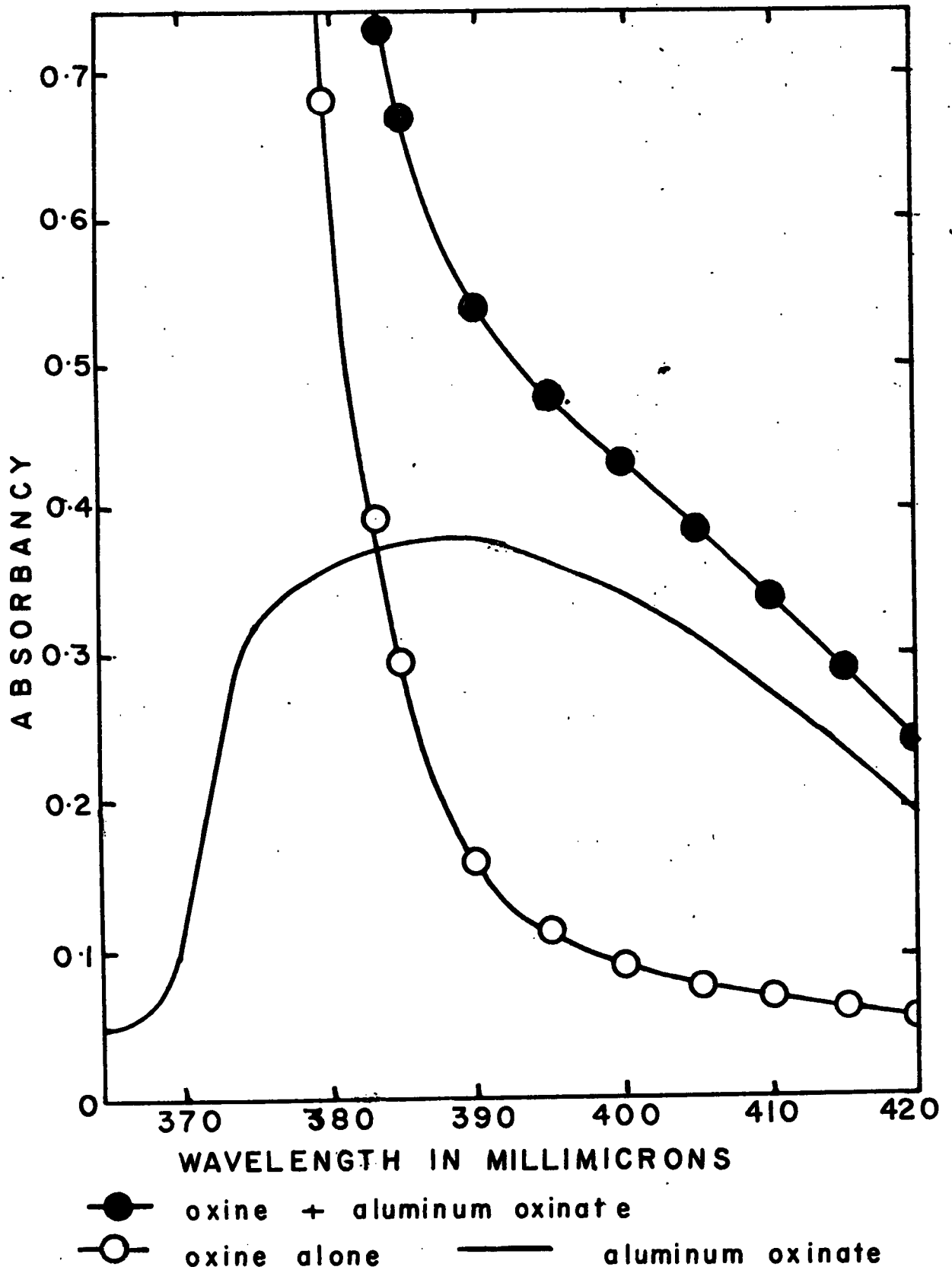
Duration of Shaking

Since there was appreciably more complete extraction after shaking for one hour than for one minute, the effect of shaking time on extraction was studied. Buffered distilled water samples of 250 ml. volume and containing 100 µg.Al/l. were shaken for various times with 5 ml. of 5% oxine, then for one minute with 5 ml. of chloroform and the combined extracts were diluted to 10 ml. with chloroform. They were compared against pure chloroform at 395 mµ and the results are shown in Table IV and Figure 2. A blank with no added aluminum was run with each sample. Ten minutes' shaking time was chosen as giving sufficiently complete extraction to be reproducible and this time was used in all subsequent extractions from acidic solution.

Table IV

Effect of duration of shaking on

extraction of aluminum oxinate.

Shaking time with oxine minutes	Absorbancy	Absorbancy – blank
1	0.438	0.365
2	0.450	0.387
4	0.463	0.400
8	0.489	0.426
15	0.509	0.446
35	0.544	0.494
60	0.589	0.526

Fig 2

Effect of shaking time on extraction of
aluminum oxinate from distilled water at
pH 4·5
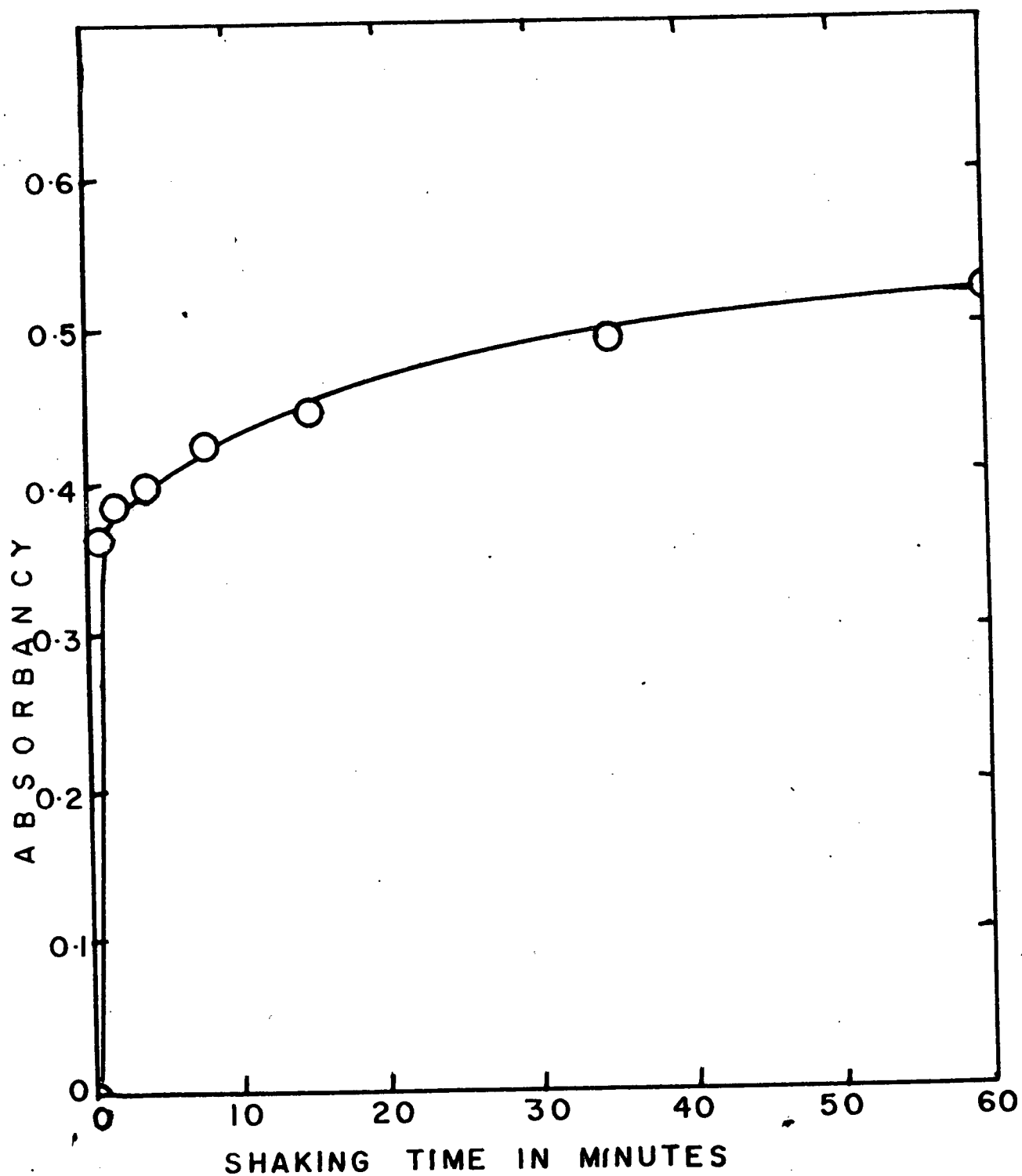
Calibration Curve

A calibration curve was prepared in distilled water as follows. Buffered samples of 250 ml. volume containing various amounts of aluminum were shaken for 10 minutes on a mechanical shaker with 5 ml. of 5% oxine. This was combined with a successive extract of 5 ml. of chloroform for one minute and then diluted to 10 ml. with chloroform. The absorbancies were compared against pure chloroform and are shown in Table V and Figure 3.

Table V

Calibration curve in distilled water

Al added µg./l	Absorbancy
0	0.058
2	0.048
5	0.059
10	0.096
20	0.129
50	0.214
100	0.494
200	1.13

Sensitivity = .0050 / µg. Al/l

Fig. 3

Calibration curve in distilled water at pH 4·5
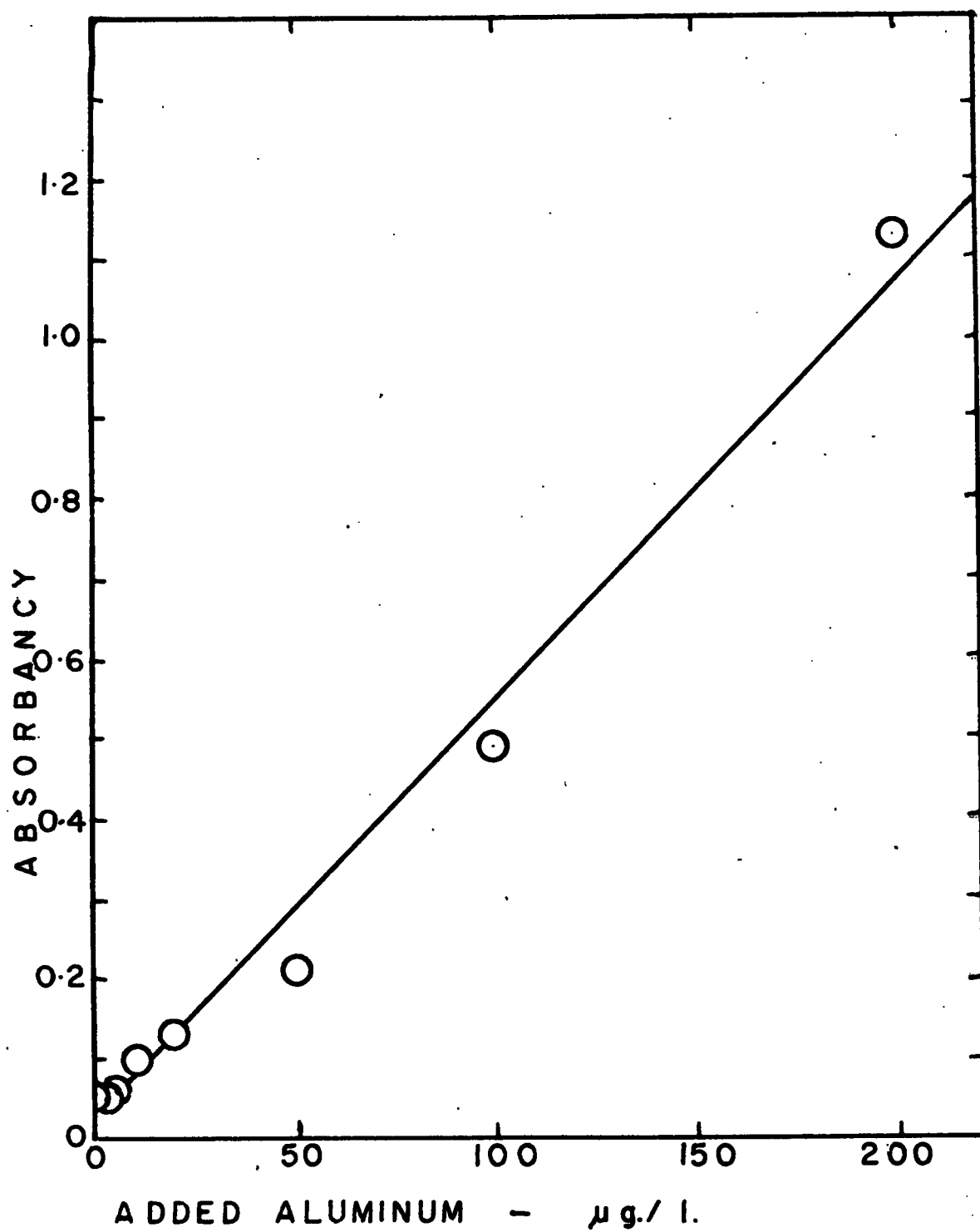
Metallic Interferences

Many cations occurring in sea water react with oxine under the conditions employed. The elements Al, Fe, Cu, Zn, Pb, U, Mo, Ag and Ni are extracted at pH 4.3-4.6 by chloroform as oxinates having absorption peaks at or near 395 mμ (20). Of these, Fe and Cu were found to be the most serious, as Table VI shows. The results in this table were obtained by adding salts of the interfering ions to buffered distilled water samples which were extracted for 10 minutes with 5 ml. of 5% oxine, and for one minute with 5 ml. of chloroform, and finally diluted to 10 ml. The ions were added as $FeCl_3 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $Pb(NO_3)_2$, $Zn(NO_3)_2$ and $UO_2(NO_3)_2 \cdot 6H_2O$.

Potassium thiocyanate partially complexed the Fe but not the Cu, as shown in Table VII. Results for this table were obtained in the same way as those for Table VI except that potassium thiocyanate was added to the samples before extraction.

A preliminary extraction with dithizone effectively removed interferences as shown in Table VIII. Buffered samples were extracted for 5 minutes with 10 ml. of a 0.01% solution of dithizone in chloroform. The aqueous extracts were washed free of dithizone with two 5 ml. portions of chloroform and finally with one 10 ml. portion of 5% oxine. These results indicate that a preliminary extraction with dithizone reduces the interference from ions other than aluminum to a negligible value.

Table VI

Absorbancies of interfering ions

Ion added	Concentration µg. /l	Absorbancy due to ion
Fe	20	0.080
Cu	10	0.100
Pb	5	0.012
Zn	5	0.005
U	1.5	0.001

Table VII

Complexing of iron and copper by potassium thiocyanate

Ion	Concentration µg. /l	Absorbancy due to ion
Distilled water 0.3M in KCNS		
Fe	20	0.010
Cu	10	0.060
Sea water 0.3M in KCNS		
Fe	20	0.006
Cu	10	0.057

Table VIII

Extraction of interfering ions by dithizone

Ion added	Concentration	Absorbancy	
	µg. /l.	Distilled water	Sea water
Fe	20		
Cu	10		
Pb	5	0.156	0.131
Zn	5		
U	1.5		
none	0	0.158	0.129
Al	100		
Fe	20		
Cu	10		0.325
Pb	5		
Zn	5		
U	1.5		
Al	100		0.339

Fluoride Interference

In addition to interfering cations, the problem of interfering anions was considered. The only serious one was fluoride which decreased the sensitivity of the method for aluminum as Table IX shows. The term sensitivity is used to designate the absorbancy of one μg.Al/l. in a sample, and can be represented as the slope of a calibration curve which obeys Beer's law. Table IX was prepared by adding various amounts of aluminum to distilled water containing sodium fluoride and extracting in the usual way with various concentrations of oxine in chloroform.

Table IX

Reduction of sensitivity by fluoride

Distilled water containing 1.5 mg. F/l.

Al added µg./l.	Oxine %	Absorbancy
100	2	0.059
	2	0.064
100	5	0.112
	5	0.103
100	10	0.272
	10	0.284

A comparison of these results with those in Table V indicates that the presence of 1.5 mg. F/1. in distilled water renders the extraction insensitive to 100 µg./1. of aluminum.

Calibration curves were prepared by adding various amounts of aluminum to buffered sea water. The sea water was then shaken for 5 minutes with 10 ml. of 0.01% dithizone, rinsed with chloroform, and the absorbancy of 10 ml. of an oxine extract was taken. The results are shown in Table X and Figure 4.

Although the results shown in Table X indicate a higher sensitivity for aluminum in sea water than in distilled water containing fluoride (Table IX) the sensitivity is lower than in distilled water (Table V), even for the highest oxine concentration used. The loss of sensitivity in sea water was presumably due to the formation of aluminum fluoride complexes. It was found (Table XI, Figure 5) that if sea water was extracted with three portions of 5% oxine before the addition of aluminum, the sensitivity for aluminum was as high as in distilled water. Results of replicate determinations are plotted in Figure 5, mean values are listed in Table XI.

Table X

Calibration curves in sea water

Al added µg./l.	Oxine %	Absorbancy
0	5	0.125
20	5	0.162
50	5	0.209
100	5	0.271

Sensitivity = 0.0015 / µg. / l.

0	10	0.194
50	10	0.274
100	10	0.359

Sensitivity = 0.0016 / µg. /l.

0	20	0.425
50	20	0.619
100	20	0.829

Sensitivity = 0.0040 / µg. / l.

Fig. 4

Effect of oxine concentration on extraction of aluminum from sea water at pH 4·5
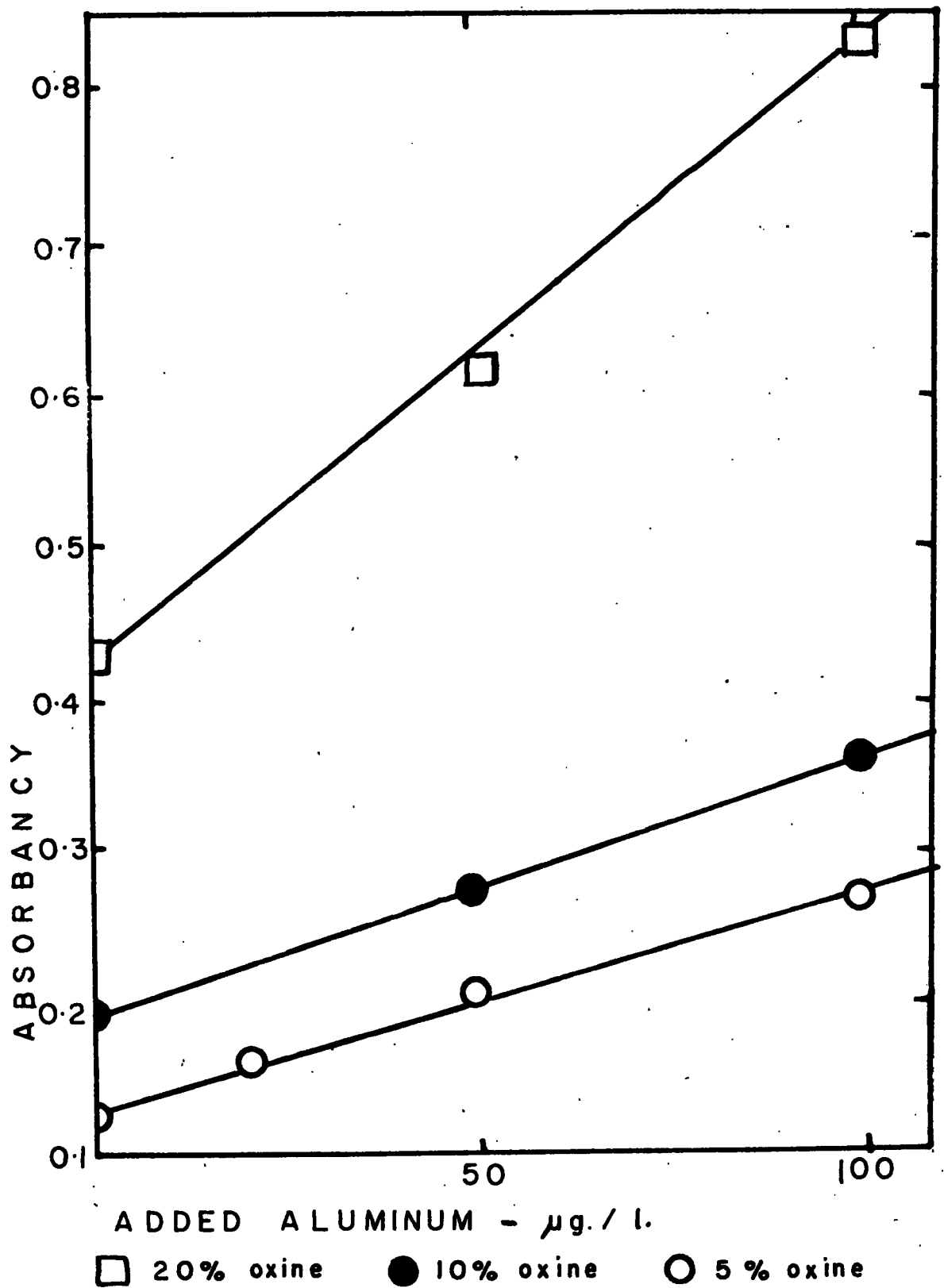
Fig. 5

Calibration curves in sea water at pH 4·5
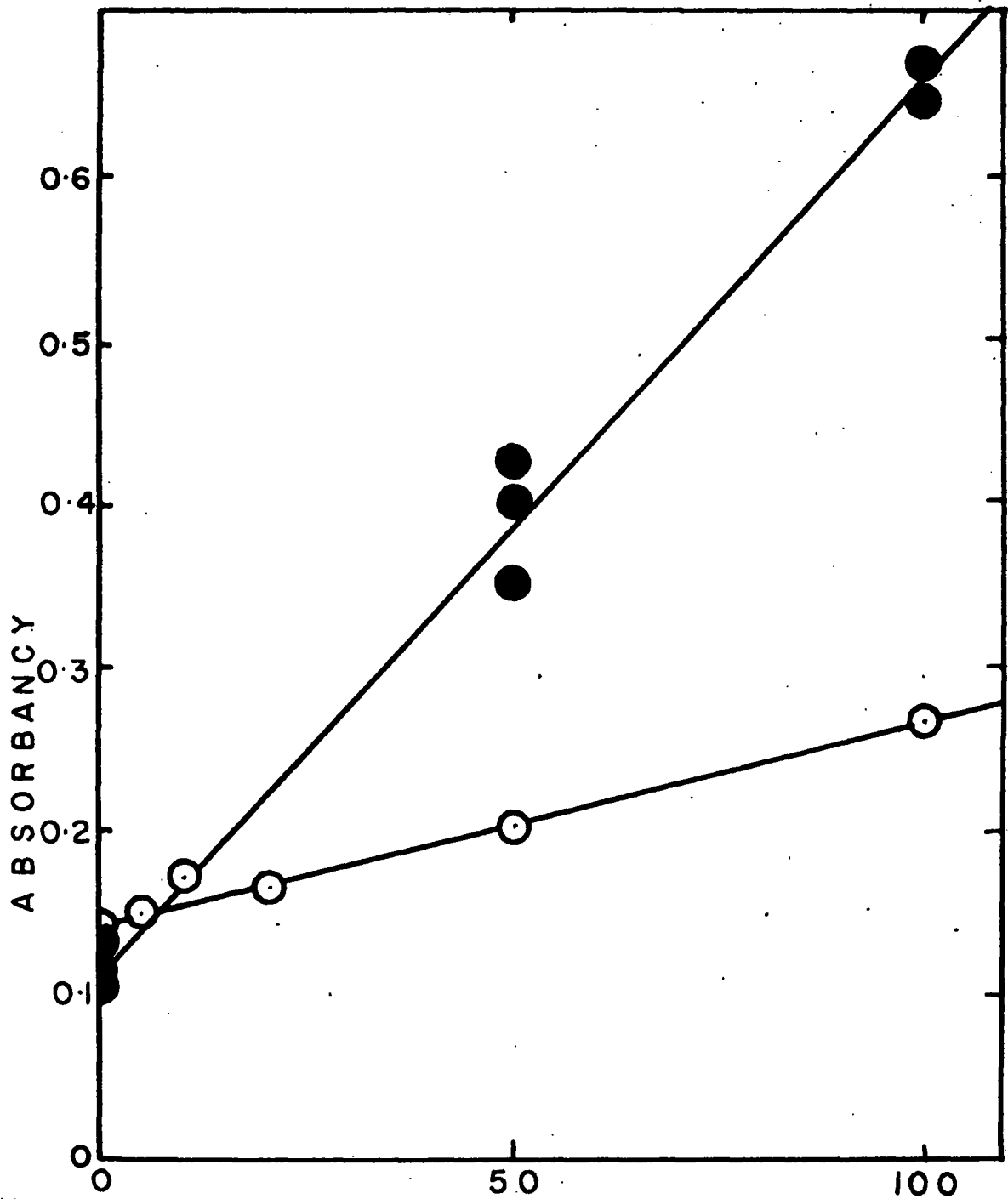
ADDED ALUMINUM — μg./l.

○ Sea water containing aluminum extracted first with dithizone, then oxine.

● Sea water extracted three times with oxine before addition of aluminum, then with oxine.

Table XI

Effect of oxine extraction before the
addition of aluminum

Order: Oxine, oxine, oxine, Al, oxine

Al added µg. /l.	Absorbancy
0	0.116
50	0.392
100	0.662

Sensitivity = 0.0052/µg./l.

Table XII

Calibration curve in sea water

Order: Al, dithizone, oxine

Al added µg. /l.	Absorbancy
0	0.140
5	0.151
10	0.171
20	0.166
50	0.200
100	0.269

Sensitivity = 0.0015/µg./l.

This sensitivity is compared with that obtained by adding aluminum to sea water and extracting with dithizone and then oxine as shown in Table XII and Figure 5.

Extraction of sea water with oxine before the addition of aluminum seemed to permit subsequent complete extraction of the added aluminum. This was further studied by extracting sea water with one portion of oxine before the addition of aluminum. The absorbancy of an oxine extract after the aluminum addition was taken. Also, sea water was treated by the following two procedures. Ten ml. of chloroform were shaken for 10 minutes with buffered sea water, then aluminum was added to the aqueous residue which was then extracted with 5% oxine. To other samples were added aluminum; the samples were then extracted with 10 ml. of chloroform, which was discarded and the aqueous residues were shaken with 5% oxine. These results are listed in Table XIII and plotted in Figure 6.

These results indicate that after a preliminary extraction with chloroform alone or with chloroform containing oxine, aluminum oxinate is more completely extracted from sea water than if this step is omitted. This effect complicates the use of dithizone in chloroform to remove interfering cations. Furthermore the effect can not be put to use in an analytical procedure for aluminum so other methods were considered for the removal of fluoride.

Table XIII

Effect of pre-extraction

Al added μg. /l.	Absorbancy

Order: 5% oxine, Al, 5% oxine

0	0.064
50	0.327
100	0.619

Sensitivity = 0.0056 / μg. / l.

Order: $CHCl_3$, Al, 5% oxine

0	0.064
50	0.210
100	0.386

Sensitivity = 0.0032 / μg. / 1

Order: Al, $CHCl_3$, 5% oxine

0	0.070
50	0.120
100	0.188

Sensitivity = 0.0012 / μg. / 1

Fig. 6

Effect of order of addition of reagents on
calibration curves in sea water at pH 4·5
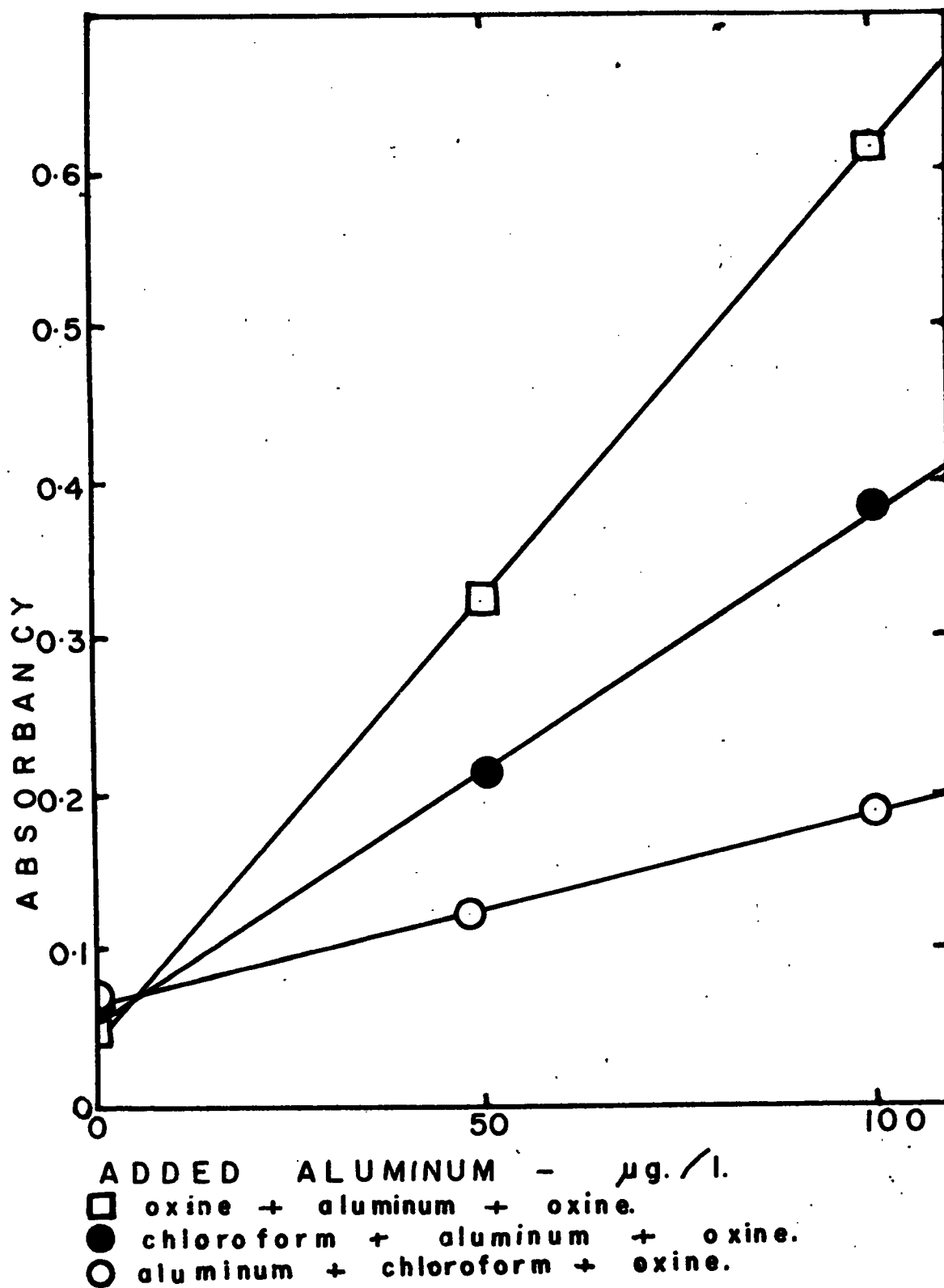
Elimination of Fluoride Interference

A procedure involving three successive extractions of aluminum oxinate from sea water with addition of oxinate absorbancies as shown in Table XIV (Figure 7) was sensitive but time consuming.

It was possible to precipitate aluminum hydroxide free from fluoride in sea water but this method also was rather tedious. Sea water containing added aluminum was added to an excess of ammonia and the centrifuged precipitate (mostly $Mg(OH)_2$) was dissolved in hydrochloric acid and diluted to 50 ml. This solution was buffered and extracted with 10 ml. of 5% oxine. Typical results are shown in Table XV. This method was not as reproducible as desired and was not used further.

An effort was made to volatilize fluoride as BF_3 by adding sodium borate and sulfuric acid to sea water and boiling the solution. This was not effective and neither was a similar attempt to volatilize SiF_4 by adding silicic acid and sulfuric acid to sea water. Nor were the results reproducible.

Table XIV

Effect of multiple extractions

Order: Al + oxine (1) + oxine (2) + oxine (3)

Al added µg. /l.	Absorbancy			
	(1)	(2)	(3)	Sum
0	0.074	0.065	0.065	0.065
50	0.158	0.138	0.132	0.298
100	0.261	0.246	0.193	0.570
Sensitivity = 0.0018/ µg./l.		0.0018/ µg./l.	0.0014/ µg./l.	0.0048/ µg./l.

Table XV

Separation of aluminum as the hydroxide

Al added µg. /l.	Absorbancy
0	0.328
25	0.499
50	0.670
100	0.719
Sensitivity = 0.006/ µg. / l.	

Fig. 7

Effect of multiple extractions from sea water at pH 4·5

ADDED ALUMINUM — µg. /l

☐ first extraction   ● second extraction

◯ third extraction   ■ sum of extractions
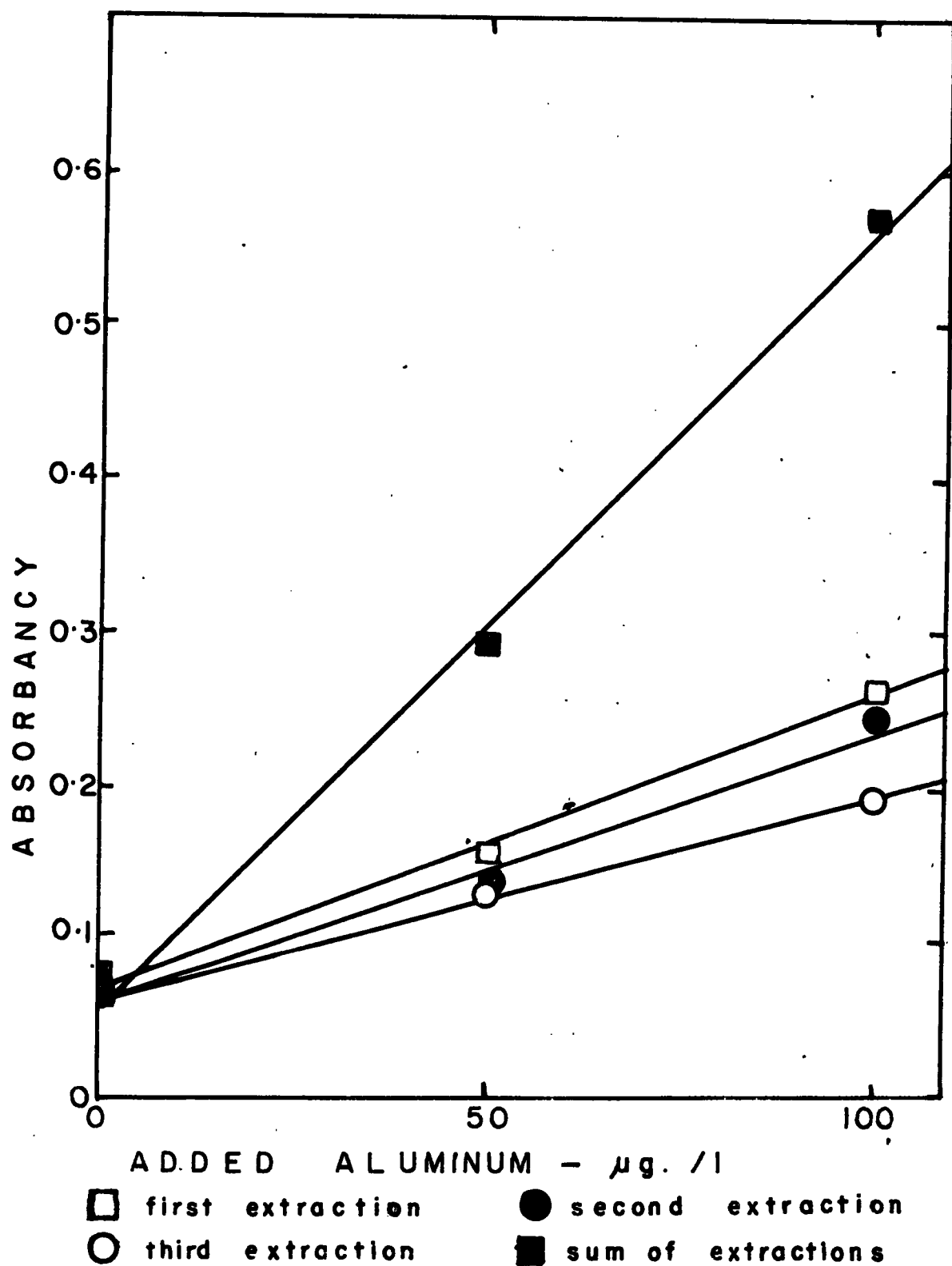
Determination of Aluminum

Although a good procedure for aluminum was not available at this point, an effort was made to establish an order of magnitude of the concentration of aluminum present in sea water. Buffered samples were shaken with 10 ml. of 0.01% dithizone for 5 minutes, rinsed with chloroform and shaken with 10 ml. of 5% oxine for 10 minutes. This extract was compared against chloroform. A blank value of 0.135, representing the contribution to the absorbancy from the reagents was subtracted from all readings. This value was obtained by extracting buffered sea water samples with 10 ml. of 5% oxine to remove any oxinate-forming metals. To the aqueous residues was added more buffer and they were then extracted with dithizone and finally with oxine as in the regular procedure. The sensitivity was taken to be 0.0015/ μg./l. (Table XII). Aluminum concentrations in 10 samples from Knight Inlet water ranged from 10-30 μg./l. However the salinity ranged from 0.28%-17.30% and variable fluoride concentrations in the less saline samples may have resulted in variable values for aluminum. The determinations were intended to give only a rough measure of the aluminum concentration.

Basic Solution

The extraction was done in basic solution and it was found that fluoride interference was not nearly so serious as in acid solution.

Effect of Fluoride

The results in Table XVI were obtained by adding sodium fluoride to samples containing aluminum. The solutions were buffered at pH 8.3 with ammonia and ammonium nitrate. They were then extracted for 10 minutes with 10 ml. of 1/2% oxine. This low concentration extracted aluminum from basic solution as satisfactorily as 5% oxine. The extracts were not diluted since nothing was gained by doing so. It was justifiably assumed that the same amount of chloroform (about 2ml.) remained dissolved in the water layer at each extraction.

Since the absorbancies of aluminum oxinate extracted from distilled water samples containing 0 and 1.5 mg. F/l. are about the same, fluoride in sea water (about 1.4 mg./l.) should not interfere seriously with the determination of aluminum. Also the sensitivity in sea water is as good as in distilled water.

Table XVI

Effect of fluoride interference

F added mg./l.	Al added µg. / l.	Absorbancy
	Distilled water	
0	0	0.080
0	100	0.685
1.5	0	0.087
1.5	100	0.700
4000	0	0.080
4000	100	0.260
	Sea water	
0	0	0.085
0	100	0.797
1000	0	0.200
1000	100	0.346

Duration of Shaking

The effect of shaking time was studied by shaking 250 ml. samples of sea water buffered at pH 8.3 and containing 100 µg. Al/l. for various times with 1/2% oxine. The absorbancies of the solutions were measured against chloroform. The blank contained no added aluminum. The results are shown in Table XVII and Figure 8.

Extraction is considerably more rapid from basic than from acidic solution (cf. Table IX and Fig. 2).

Two minutes shaking time was chosen as giving sufficiently complete extraction to be reproducible. All succeeding samples were shaken manually for two minutes with 1/2% oxine and the extracts were compared without dilution with chloroform.

Effect of pH

Since magnesium oxinate is formed at pH9 but is not extracted by chloroform (7), a study was made of the effect of pH on extraction of aluminum oxinate from sea water. Buffered sea water samples containing added aluminum were shaken with 10 ml. of 1/2% oxine. The blanks contained no added aluminum. Typical results are shown in Table XVIII and Figure 9.

Table XVII

Dependence of extraction in basic
solution on duration of shaking.

Shaking time seconds	Absorbancy	Absorbancy -- blank
10	0.541	0.461
30	0.658	0.578
60	0.720	0.640
120	0.772	0.692
300	0.798	0.718

Fig. 8

Effect of duration of shaking on extraction

from sea water at pH 8·3
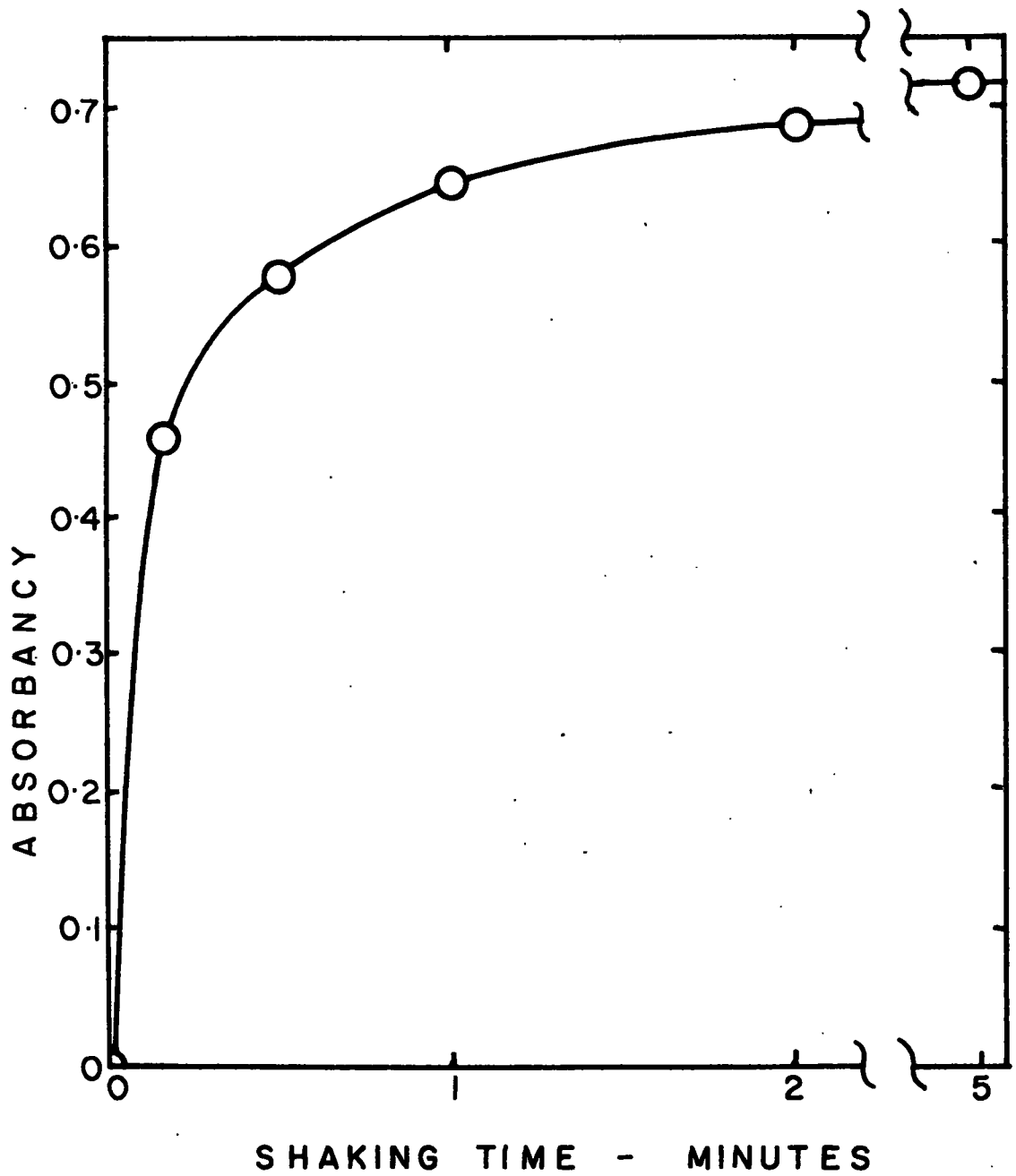
Table XVIII

Effect of pH on extraction of aluminum

oxinate from sea water

Final pH	Absorbancy no added Al	Absorbancy 100 µg.Al/l.added
6.90	0.125	0.389
7.15	0.116	0.564
7.58	0.129	0.790
7.72	0.139	0.797
7.85	0.126	0.812
8.21	0.140	0.750
8.38	0.148	0.799
8.80	0.171	0.840
9.05	0.207	0.580
9.30	0.262	0.308
9.60	0.508	0.480
10.0	> 2	> 2

Sensitivity at pH 8.0 = 0.0070 / µg. / l.

These results showed pH 8 to be the best for extraction of aluminum oxinate.

An experiment similar to the previous one was done by extracting distilled water samples, some containing added magnesium, with 1/2% oxine for two minutes. The effect of pH on such extractions is shown in Table XIX and in Figure 10.

Table XIX shows that the formation of magnesium oxinate can account for the lack of extraction of aluminum oxinate at above pH 9.5. All subsequent samples were buffered at pH 7.8 - 8.2 by the addition of one ml. of a buffer which made the final solution 0.04M in NH_4NO_3 and 0.002M in NH_3.

Cation Interference

Several methods were attempted for the removal of interfering cations. The ions in sea water which interfere at pH 8 are Fe, Cu, Mn, Pb, Zn and U (7). The contributions to absorbancy from various ions added to distilled water at pH 8 are shown in Table XX.

As Table XX shows, copper and manganese were the most serious interferences in basic solution. Potassium cyanide formed a copper complex in solution. Potassium permanganate could not be used to oxidize manganese as there was always some unoxidized manganese left to give an oxine reaction. Periodic acid oxidized manganese but

its addition to sea water caused precipitation, and reduced the sensitivity of the aluminum reaction. As Table XXI shows, one mg. of periodic acid and 5 mg. of potassium cyanide in a 250 ml. sample of sea water reduced the absorbancy of interfering cations to about 0.015.

The sensitivity for aluminum in the presence of periodic acid is shown in Table XXII. The results were obtained in the same way as those in Table XXI, and by adding various amounts of aluminum to sea water containing periodic acid. These results showed that periodic acid could not be used to oxidize manganese in the procedure for aluminum. Manganese could not be complexed by potassium cyanide in reducing solution as shown by the results in Table XXIII. This table was prepared by adding salts of interfering ions to buffered sea water containing 5 mg. of potassium cyanide per 250 ml. and 0.25 gm. of sodium thiosulfate per 250 ml. followed by extraction in the usual way.

Table XIX

Effect of pH on extraction of aluminum oxinate from distilled water and magnesium chloride solution.

Final pH	Absorbancy no added Al	Absorbancy 100 µg./l. added
Distilled water		
6.41	0.052	0.271
7.10	0.075	0.749
7.50	0.088	0.810
7.81	0.074	0.785
8.50	0.095	0.810
9.00	0.130	0.840
9.60	0.059	0.721
9.88	0.108	0.738

Sensitivity at pH 8 = 0.0070 / µg. / l.

Distilled water containing 5 gm. $MgCl_2$ / l.

9.15	0.159	0.491
9.50	0.177	0.350
9.95	0.420	0.327

Fig. 9

Effect of pH on extraction of aluminum oxinate from sea water

ABSORBANCY

FINAL pH OF SOLUTION

○ sea water
● sea water + 100 μg. Al / l.
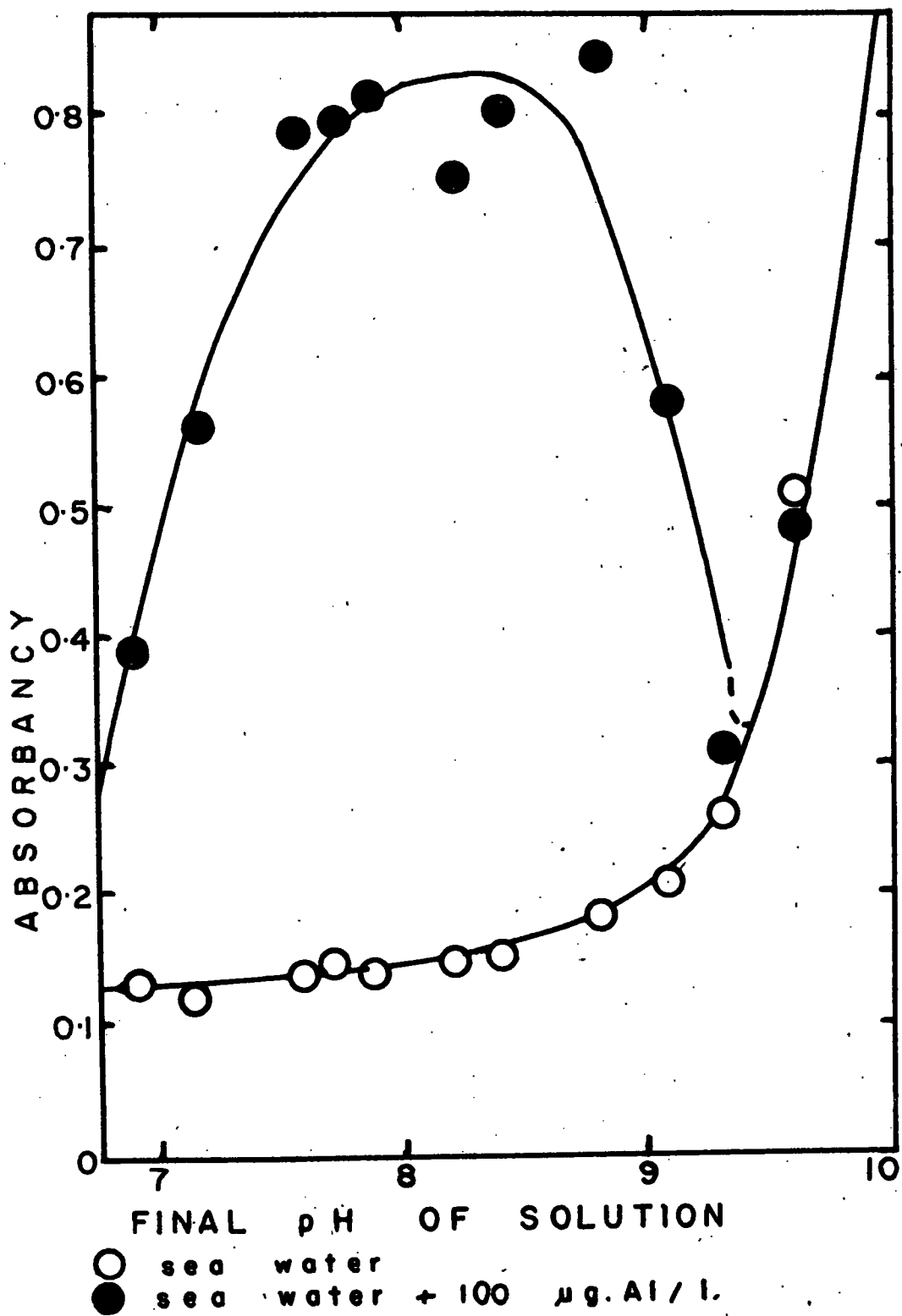
Fig. 10
Effect of pH on extraction of aluminum oxinate
from distilled water containing MgCl$_2$.

FINAL pH OF SOLUTION
○ distilled water   ● distilled water+100μg.Al/l.
□ distilled water + 5 g.MgCl$_2$/l.
■ distilled water + 5 g.MgCl$_2$/l. + 100μg.Al/l.
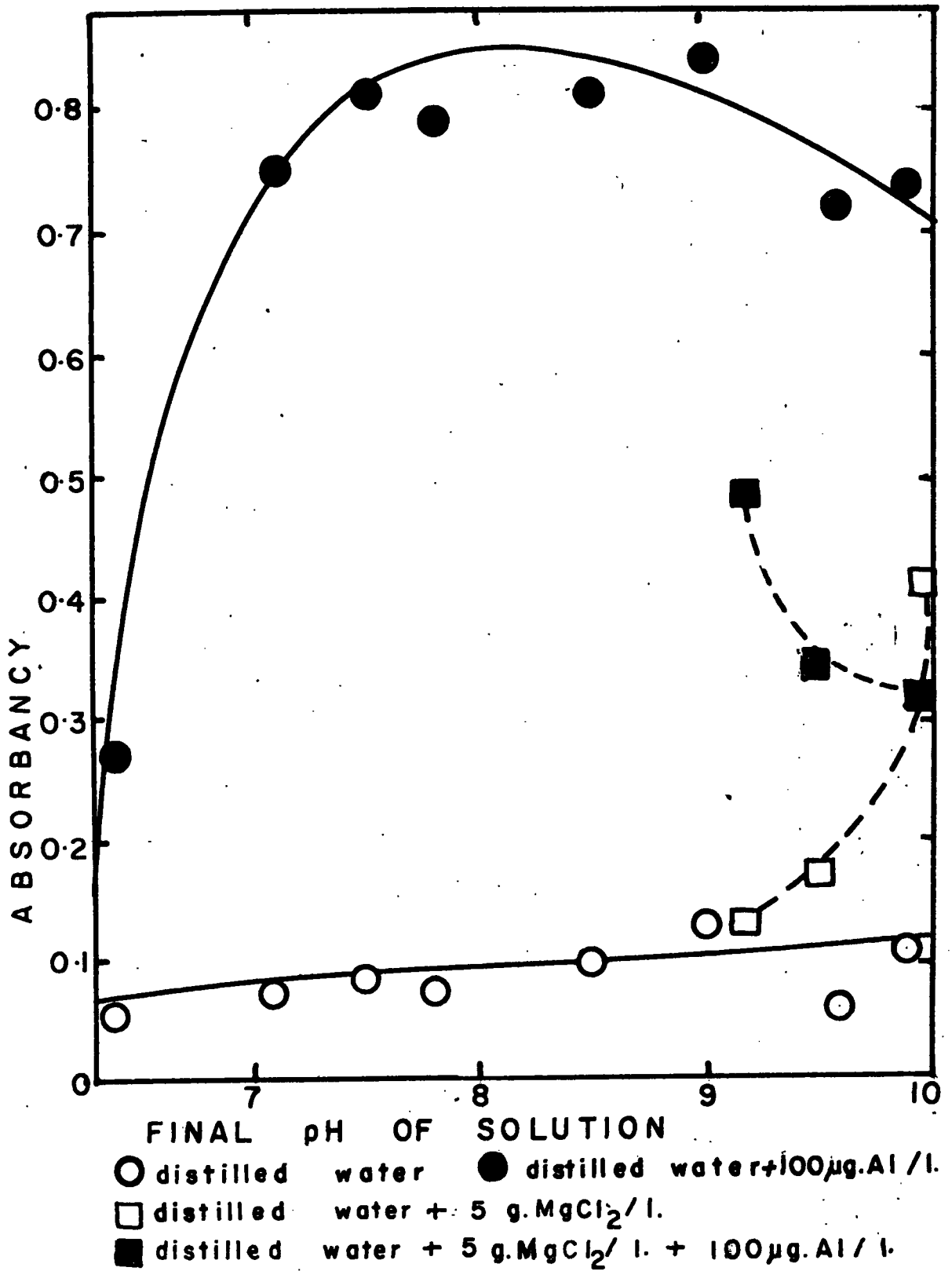
Table XX

Contributions of ionic interferences

Ion	Concentration	Absorbancy
Fe	20	.004
Cu	10	.021
Mn	10	.042
Pb	5	.003
Zn	5	.002
U	1.5	.003

Table XXI

Absorbancy of interfering ions

in the presence of H_5IO_6 and 5 mg. of KCN

Ion	Concentration $\mu g. / l.$	H_5IO_6 mg./250ml.	Absorbancy
Mn	10	1	0.015
Cu	10	1	0.007
Fe	20		
Mn	10		
Cu	10		
Zn	5	1	0.012
Pb	5		
U	1.5		
Mn	10	0.01	0.040
Fe	20		
Cu	10		
Mn	10	0.01	0.083
Zn	5		
Pb	5		
U	1.5		

Table XXII

Effect of periodic acid on

sensitivity for aluminum

H_5IO_6 added mg. / 250 ml.	Sensitivity for Al
1	0.0014 - 0.0035
0.1	0.0043 - 0.0066
0.01	0.0064

Table XXIII

Effect of interfering cations in

reducing cyanide solution.

Ion	Concentration μg. / l.	Absorbancy due to ion
Fe	20	0
Cu	10	0
Mn	10	0.045
Pb	5	0.002
Zn	5	0.002
U	1.5	0.003

Removal of Manganese Interference

Manganese oxinate is not extracted from acidic solution (7), so a back-extraction technique was used whereby manganese oxinate was extracted from the chloroform layer into acidic distilled water. Buffered samples containing potassium cyanide and sodium thiosulfate were extracted with 1/2% oxine in the usual way. The chloroform extract was then shaken for one minute with 50 ml. of distilled water kept at pH 4.3-4.6 with acetate buffer. This time was found to give as complete extraction as possible. Some solutions containing added manganese and others containing in addition some of the other trace metals in concentrations listed in "The Oceans" (23, p. 176) were treated in this way. The results are shown in Table XXIV. Table XXIV showed manganese interference to be satisfactorily reduced by back-extraction. There was no effect on the sensitivity for aluminum as can be seen from the calibration results shown in Tables XXV and XXVI, and in Figures 11 and 12.

Table XXIV

Removal of manganese by back-extraction

Ion	Concentration μg. / l.	Absorbancy due to ion
	Distilled water	
Mn	10	0.025
Fe III	20	
Cu II	10	
Mn II	10	0.025
Pb II	5	
Zn II	5	
U VI	1.5	
Mn	10	0.016
Fe III	20	
Mn II	10	
Cu II	10	0.012
Pb II	5	
Zn II	5	
U VI	1.5	

Back-Extraction Procedure

The values for the calibration curves were obtained by extracting 250 ml. samples, containing various amounts of aluminum and buffered at pH 7.8-8.2, for two minutes with 1/2% oxine in chloroform. The chloroform extracts were then shaken for one minute with 50 ml. of distilled water buffered at pH 4.3-4.6. Blank values for samples containing no aluminum were obtained by extracting buffered samples for five minutes with 10 ml. of 1/2% oxine. The extracts were drawn off and the aqueous residues rinsed with three 2 ml. portions of chloroform to remove the remaining oxine. These samples were then treated with buffer, potassium cyanide and sodium thiosulfate and shaken with 8 ml. of 1/2% oxine (the volume not retained by chloroform after the initial extraction).

They were then back-extracted and then absorbancy read against chloroform. The values for distilled water samples were 0.026 and 0.026. The values for sea water samples were 0.018, 0.030, 0.015, and 0.018. Absorbancies for standard curves were corrected so that those for samples containing no added aluminum equalled the blank values above.

Table XXV

Calibration curve in distilled water

using back-extraction procedure

Al added µg. /l.	Absorbancy	Corrected Absorbancy
0	0.045	0.026
10	0.115	0.096
20	0.182	0.163
30	0.280	0.261
40	0.334	0.315
50	0.421	0.407

Fluoride added = 1.5 mg. / l.

20	0.195	0.176
50	0.426	0.407

Sensitivity = 0.0075 / µg. Al / l.

Fig. II

Calibration curve in distilled water using back-extraction procedure

Calibration curve in distilled water using back-extraction procedure

ABSORBANCY vs ADDED ALUMINUM — μg./l.

○ distilled water.
● distilled water + 1·5 mg.F/l.
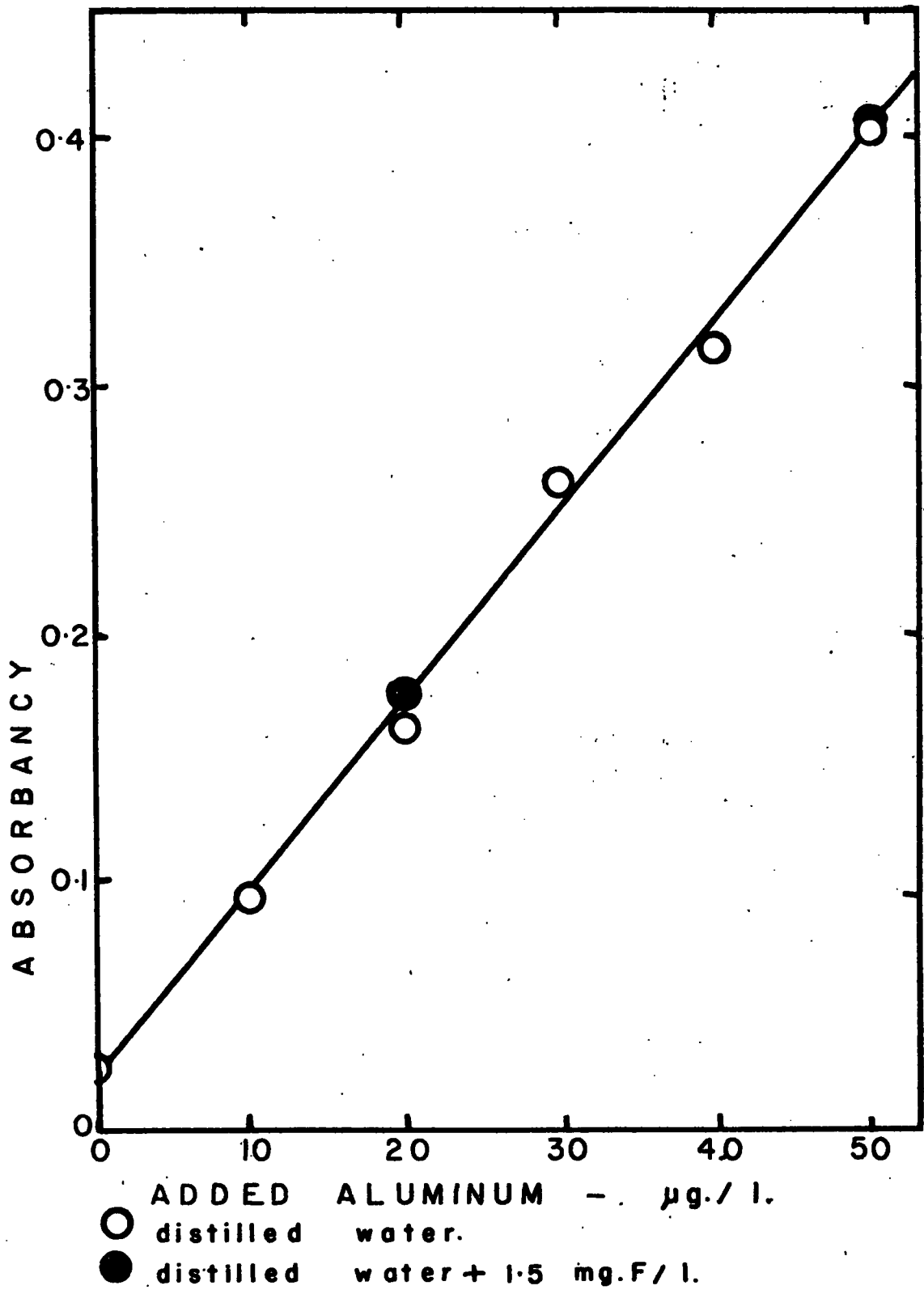
Fig. 12

Calibration curve in sea water using back-extraction procedure
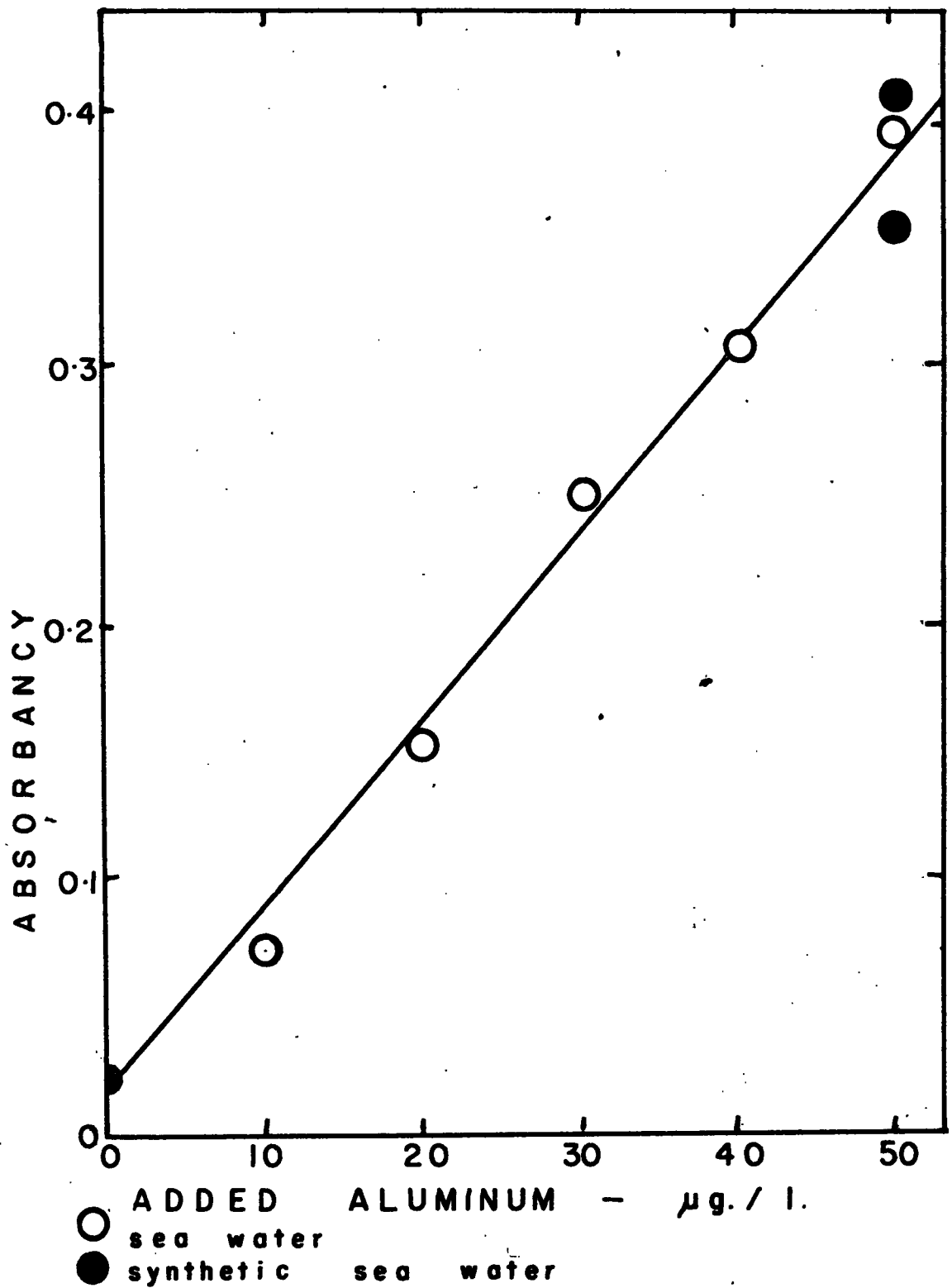
Table XXVI

Calibration curve in sea water using
back-extraction procedure.

Al added µg./l.	Absorbancy	Corrected Absorbancy
0	0.115	0.020
10	0.165	0.070
20	0.248	0.153
30	0.344	0.249
40	0.402	0.307
50	0.485	0.390

Synthetic sea water

0	0.135	0.020
50	0.514	0.378

Sensitivity = 0.0075 / µg. Al / l.

Final Procedure

The back extraction procedure was applied to aluminum determination in sea water. Sea water samples of 250 ml. volume were treated with two ml. of a solution containing 0.25 gm. $Na_2S_2O_3$, 5 mg. KCN, 0.71 gm. NH_4NO_3, and 0.25 M in NH_3. These were shaken manually for two minutes with 10 ml. of 1/2% oxine, and the chloroform extracts were shaken for one minute with 50 ml. of distilled water 0.01M in ammonium acetate and 0.02M in acetic acid. The absorbancies of the extracts were then compared with chloroform at 395 mμ. The aluminum concentrations corresponding to the measured absorbancies were read from Figure 12.

The concentration of aluminum in surface water taken from Departure Bay (absorbancy 0.115) was thus 14 μg./l. Values of aluminum concentration in ocean samples are reported in Tables XXVII - XXXIII and are plotted in Figures 13-16. In the first column of these tables, the salinity is listed in parts per thousand ($^o/oo$).

In addition to the deep sea determinations reported in Tables XXVII--XXXIII some determinations were done on surface samples from inlet coastal water. The coastal results are reported in Table XXXIV. The dates of sampling were between 2-VII-55 and 12-VII-55.

Fig. 13

Vertical distribution of aluminum
in sea water
Lat. 54° 15'N   Long. 142° 41' W
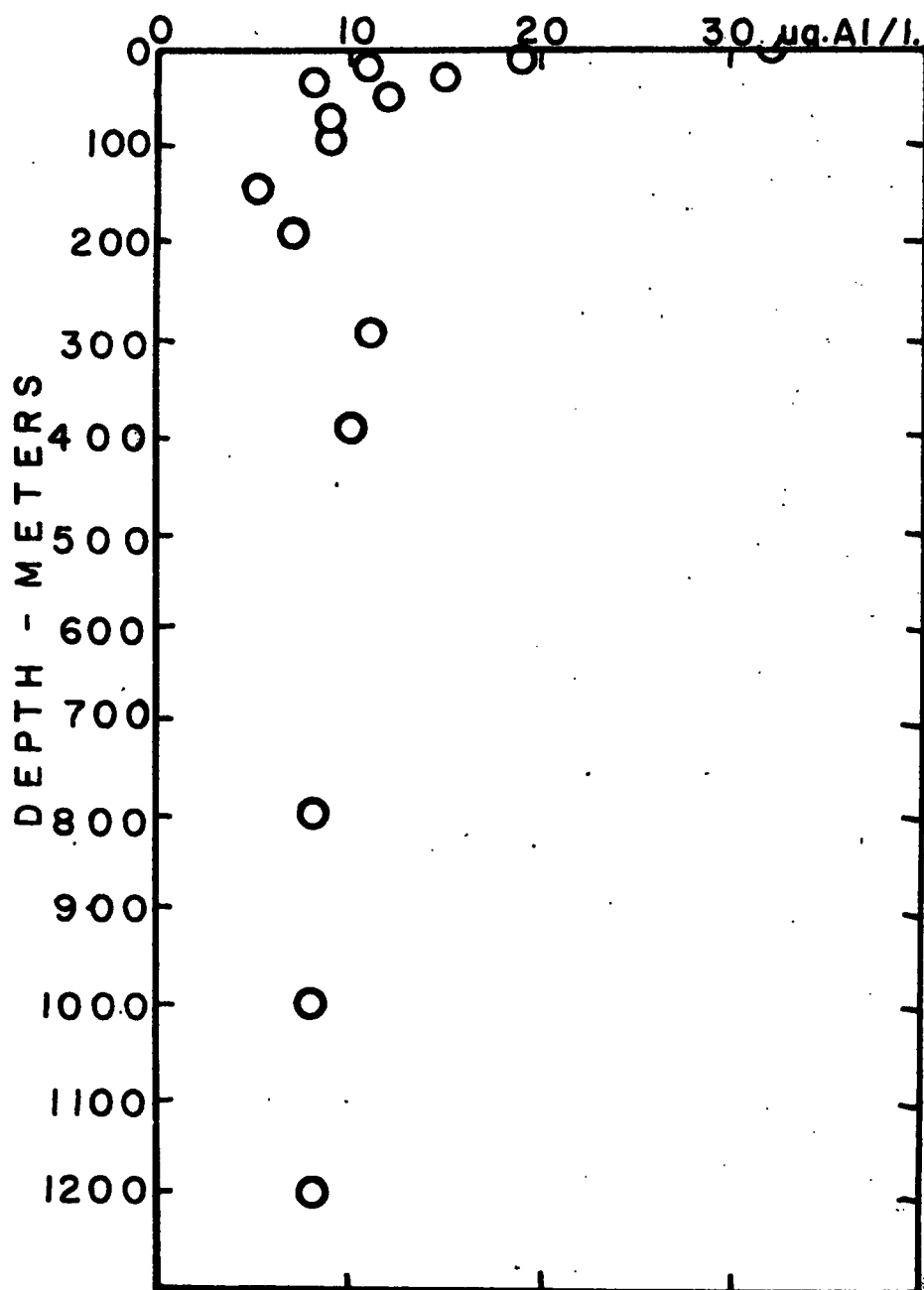
Fig. 14
Vertical distribution of aluminum
in sea water
Lat. 54° 19' N   Long. 144° 41' W
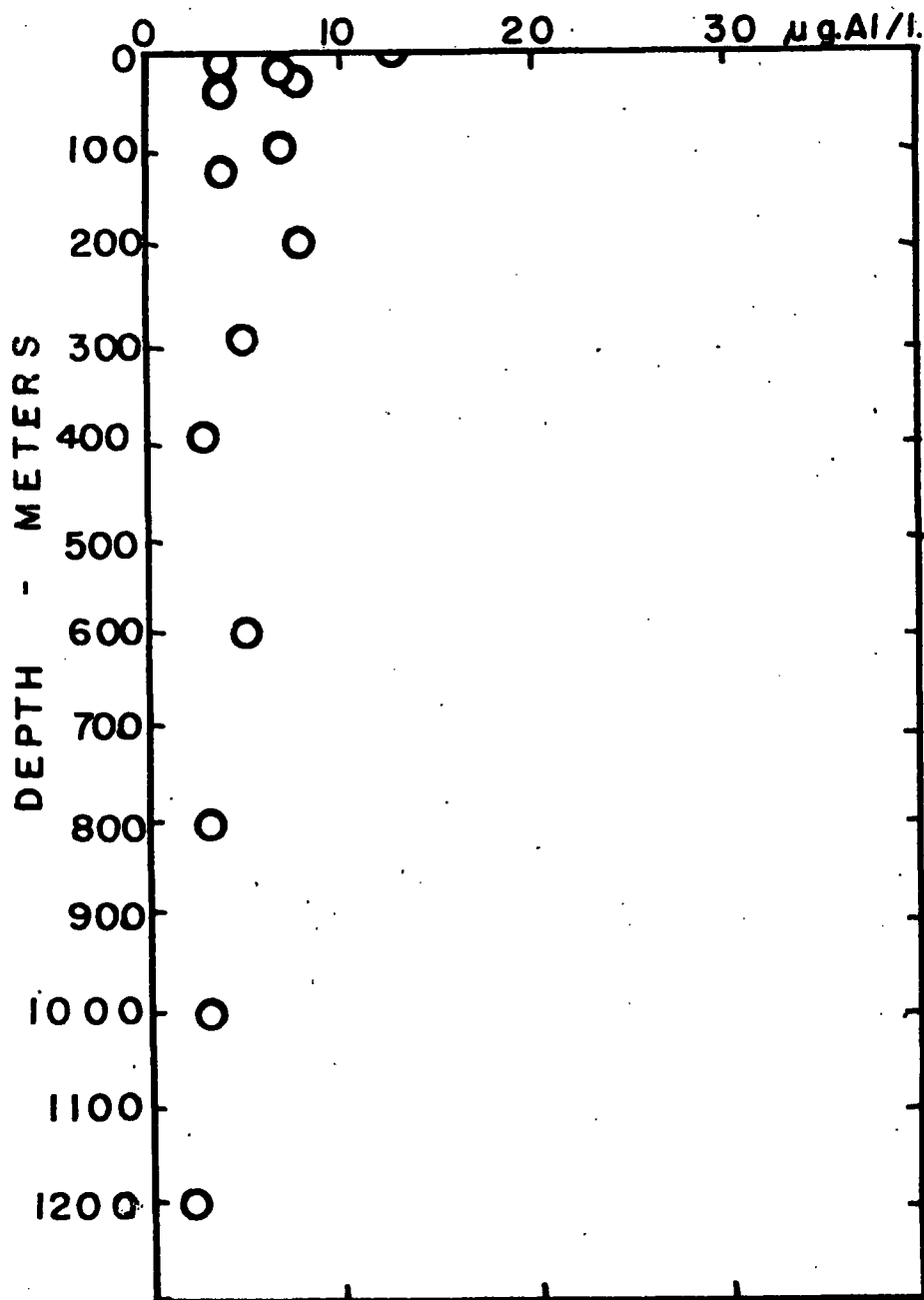
Fig. 15

Vertical distribution of aluminum

in sea water

Lat. 53° 13' N   Long. 160° 53' W
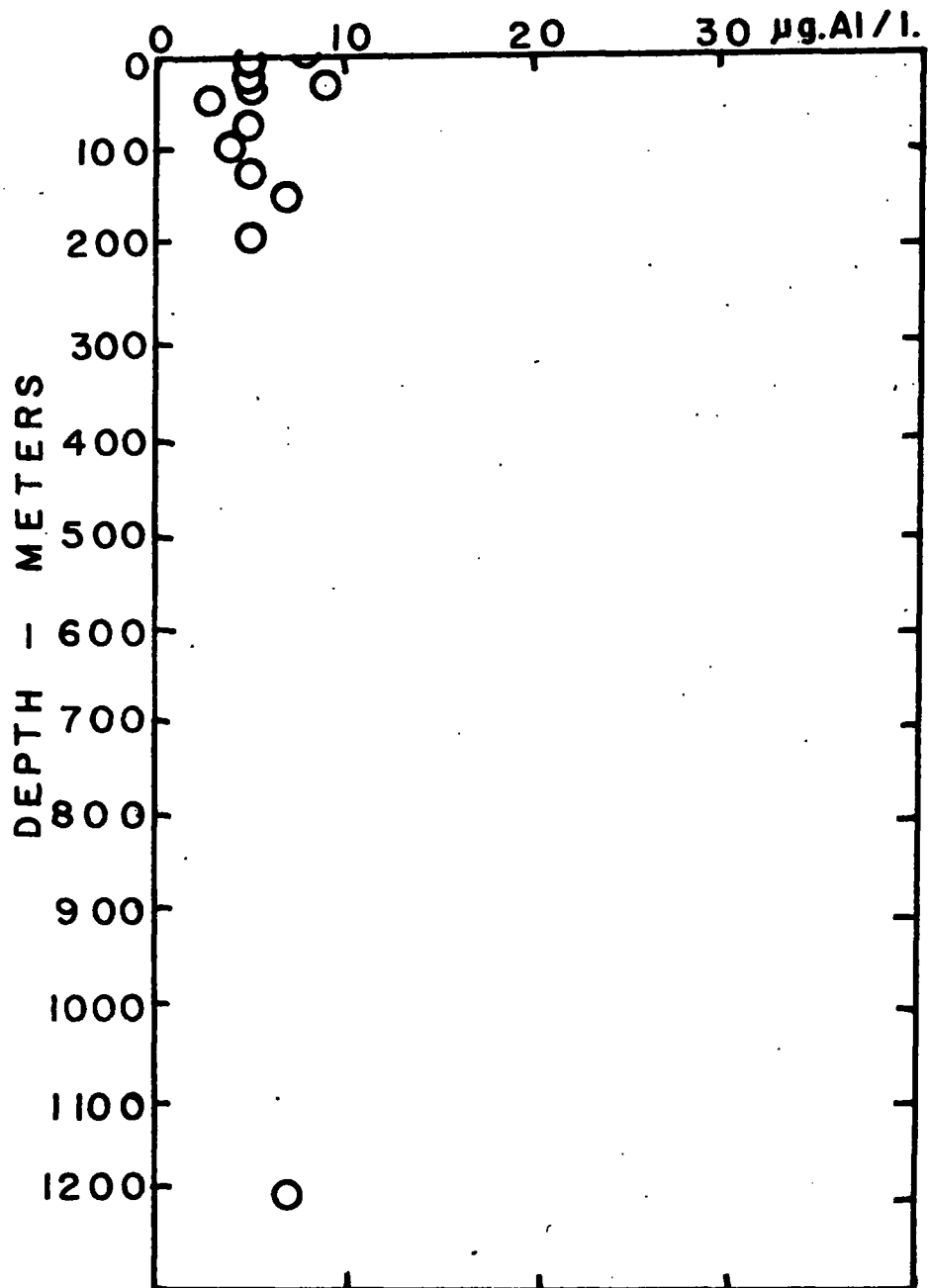
Fig. 16

Vertical distribution of aluminum

in sea water

Lat. 51° 51' N   Long. 146° 37' W
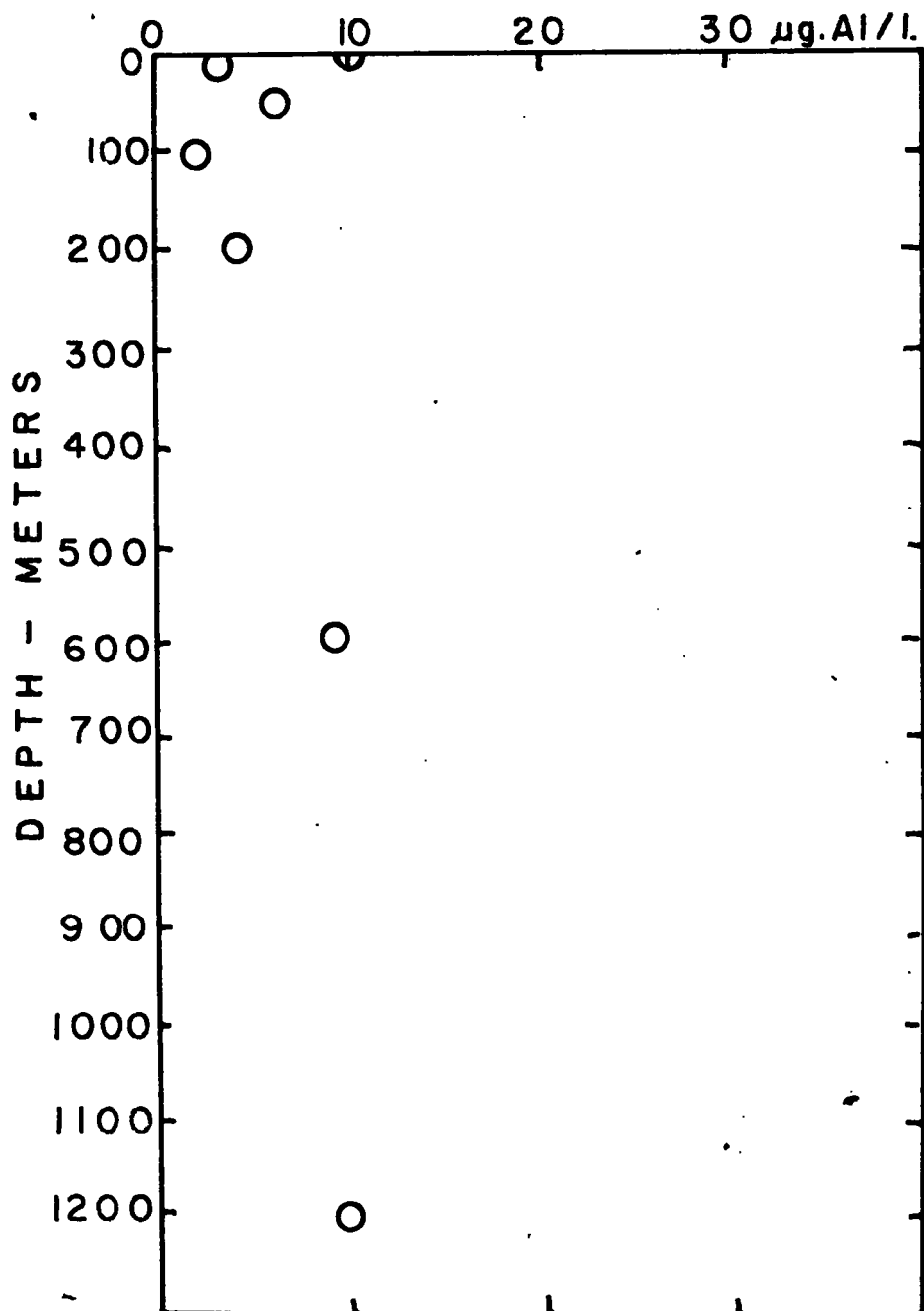
Table XXVII

Vertical distribution of aluminum

Lat. 54° 15'N   Long. 142° 41'W

Date of sampling 3-VIII-55

S °/oo	Depth meters	Absorbancy	Al concentration µg. / l.
32.67	0	0.257	32
32.58	10	0.161	19
32.60	20	0.100	11
32.65	30	0.135	15
32.67	40	0.078	7
32.71	50	0.113	12
32.79	75	0.090	9
33.14	100	0.085	9
33.79	150	0.060	5
33.86	200	0.076	7
33.94	300	0.100	11
34.05	400	0.094	10
34.29	800	0.084	8
34.37	1000	0.077	8
34.44	1200	0.075	8

Table XXVIII

Vertical distribution of aluminum

Lat. 54°19'N   Long. 144°41'W

Date of sampling 4-VIII-55

S ‰	Depth meters	Absorbancy	Al concentration µg. / l.
32.74	0	0.119	13
32.74	10	0.050	4
32.76	20	0.068	7
32.79	30	0.077	8
32.81	40	0.052	4
32.96	100	0.063	7
33.31	125	0.053	4
33.72	150	0.062	7
33.87	200	0.074	8
33.96	300	0.058	5
34.01	400	0.045	3
34.20	600	0.058	5
34.30	800	0.038	3
34.38	1000	0.035	3
34.46	1200	0.034	2

Table XXIX

Vertical distribution of aluminum

Lat. $53°13'N$ Long. $160°53'W$

Date of sampling 7-VIII-55

S $°/_{oo}$	Depth meters	Absorbancy	Al concentration µg. / l.
32.41	0	0.079	8
32.38	10	0.060	5
32.38	20	0.055	5
32.40	30	0.085	9
32.65	40	0.058	5
32.78	50	0.042	3
33.03	75	0.061	5
33.41	100	0.053	4
33.69	125	0.054	4
33.88	150	0.068	7
34.00	200	0.058	5
34.48	1200	0.070	7

Table XXX

Vertical distribution of aluminum

Lat. 51°51'N   Long. 146°37'W

Date of sampling 30-VIII-55

S ⁰/₀₀	Depth meters	Absorbancy	Al concentration μg. / l.
32.90	0	0.097	10
32.86	10	0.039	3
32.84	50	0.064	6
33.07	100	0.035	2
33.86	200	0.047	4
34.24	600	0.089	9
34.40	1000	0.093	10

Table XXXI

Vertical distribution of aluminum

Lat 54°26'N   Long. 158°07'W

Date of sampling 16-VIII-55

S ⁰/₀₀	Depth meters	Absorbancy	Al concentration μg. / l.
32.22	0	0.093	10
32.15	10	0.063	6
32.84	50	0.061	5
33.10	100	0.053	5

Table XXXII

Vertical distribution of aluminum

Lat. 52°04'N   Long. 160°44'W

Date of sampling 17-VIII-55

S ⁰/oo	Depth meters	Absorbancy	Al concentration µg. / l.
32.31	0	0.185	22
32.24	10	0.096	10
32.58	50	0.060	5

Table XXXIII

Vertical Distribution of aluminum

Lat. 47°01'N   Long.135°16'W

Date of sampling 30-VIII-55

S ⁰/oo	Depth meters	Absorbancy	Al concentration µg. / l.
32.65	0	0.094	10
32.62	10	0.054	5
33.75	200	0.078	8
34.12	600	0.057	5

Table XXXIV

Aluminum concentration in surface coastal water.

Inlet	S $^o/_{oo}$	Absorbancy	Al concentration µg. / l.
Bute	14.43	0.227	27
	7.27	0.178	21
	6.50	0.185	22
	3.66	0.136	15
	3.13	0.147	17
	1.81	0.109	12
	0.73	0.097	10
Toba	8.91	0.305	37
	6.68	0.176	21
	2.47	0.093	10
Knight	17.93	0.221	26
	9.81	0.345	42
Longborough	15.57	0.208	25
	5.52	0.162	19
Wakeman	0.53	0.244	29
Thompson Sound	14.38	0.171	20

The samples containing high aluminum concentrations were quite fluorescent under ultra violet light, while those low in aluminum exhibited no noticeable fluorescence.

The deep sea samples were collected in brass sampling bottles and were stored in glass bottles. Surface samples were collected in a canvas bucket. The inlet samples were stored in polyethylene bottles.

DISCUSSION

The molar absorptivity is a measure of the sensitivity of a color reaction and is written as

$$k = \frac{A}{C \; l} \quad , \text{ where}$$

A = absorbancy

C = molar concentration of colored product

l = path length in cm.

For the reagent used it was found that 0.25 µg. of aluminum in 8 ml. chloroform gave an absorbancy of 0.0075, assuming complete extraction (See Figure 12). The concentration of aluminum in the chloroform layer was 11.5×10^{-7}M. For the one cm. cells used the value of k was $\dfrac{0.0075}{11.5 \times 10^{-7} \times 1} = 6500$

After extraction, the effective value of k was

$$\frac{6500 \times 250}{8} = 200,000.$$

The behavior of acidic solutions containing fluoride which were extracted with chloroform before the addition of aluminum needed explanation. The increased sensitivity for aluminum of such solutions indicates that the chloroform removes something that interferes with the extraction of aluminum oxinate. The interference might possibly be fluoride in the form of hydrogen fluoride. It is unlikely that any aluminum fluoride complex was extracted since this suggestion does not agree with the results shown in Figures 4 and 7. Much aluminum could not have been removed by the chloroform since subsequent oxine extractions removed the greater part of it.

Aluminum in a concentration of 100 µg. / l. was not extracted by oxine at about pH 7 although the solubility product for aluminum hydroxide was not exceeded. This may have been due to the formation of the aluminum fluoride complex. At a higher pH the aluminate ion is formed and the oxine apparently competes more favorably than fluoride for the aluminum in this ion.

At a pH of about 9.5 in sea water magnesium oxinate is formed but becomes hydrated on shaking and remains in the water layer. This accounts for the lack of extraction of aluminum oxinate from sea water at pH 9.5 (Figures 11 and 12); the magnesium combines with all the available oxine. Above pH 9.5 magnesium oxinate is extracted into the organic layer; it is not known whether it remains hydrated. The extraction accounts for the increase in the blank value with increasing pH (Figure 11). Above about pH 10.5 precipitation of magnesium hydroxide takes place.

Some natural sea water samples yielded a white foam at the liquid-liquid interface during shaking. This may have been caused by organic matter acting as an emulsifying agent, since it was not observed in synthetic sea water.

The back-extraction procedure for the removal of manganese was not quite complete as shown by comparison of absorbancies of Table XXI with those of Table XXIV. This may have been due to back-extraction of manganous oxinate being slow.

Potassium cyanide was very effective in complexing copper as Cu $(CN)_3^=$ and iron as $Fe(CN)_6^{\equiv}$. Manganese forms a complex cyanide, $Mn(CN)_4^=$ (6) but this may be less stable than the manganese oxinate.

The determinations indicated aluminum concentrations in sea water of from 0 - 40 µg. / l. Even the upper limit does not exceed the solubility product of aluminum hydroxide (26) at the normal pH of sea water which is 7.5 - 8.4 (23, p. 195). If one accepts the value of 10^{-22} (26) for the solubility product of aluminum hydroxide the aluminum ion concentration must be 10^{-4} M at pH 8 before precipitation can take place. Sea water is therefore apparently unsaturated in aluminum hydroxide.

The somewhat higher values of aluminum in inshore samples than in deep sea samples may indicate that some process removes aluminum at the river mouths.

In general, the surface samples of oceanic water were higher in aluminum content than the deeper samples, (Figures XXVII - XXXIV).

The calibration curves (Figures 11 and 12) indicate an error of not more than ± 3 µg. Al / l. in this procedure. The contribution from interfering ions may make the results high by as much as 3 - 5 µg. Al / l. (Table XXIV).

CONCLUSION

A comparison of the various values reported for aluminum in sea water is given in Table XXXV (8,14,22,24).

The values reported for aluminum in the present work represent only ionic aluminum or that adsorbed aluminum which will react with oxine under the conditions used. Aluminum strongly adsorbed on clay particles may not react under these conditions nor should any aluminum that is an integral part of the clay structure.

The results listed here represent an upper value for the available aluminum since traces of some metals may have come from sampling apparatus and have been incompletely removed in the procedure followed.

The average value for 16 coastal samples was 23 μg. Al / l ; that for 50 oceanic samples was 7 μg. Al / l.

It is doubtful if too much reliance can be placed on some of the higher values reported by various workers. It seems unlikely that the aluminum concentration in sea water should show such a large variation as reported in Table XXXV.

Table XXXV

Concentration of aluminum in sea water

Concentration of Al µg. / l.	Location	Reagent	Reference
600 - 2400	Pacific coast	aluminon	(24)
160 - 1800	Pacific coast	oxine	(8)
295 - 325	Japanese coast	aluminon	(14)
0 - 7	Atlantic coast	Pontachrome Blue Black R	(22)
2 - 42	Pacific coast	oxine	present work

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