

STUDIES ON THE ORGANIC HALOGEN COMPOUNDS
IN SEA WATER

by

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SUMMARY

A literature survey as well as an experimental search to enable better estimation of the possible role of the organic halogen compounds in the geochemical cycle of the halogens has been done. A tentative procedure for measuring organic halogen compounds has been outlined and possible future experiments suggested.

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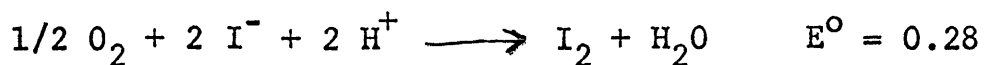
(I) Introduction

The geochemistry of halogens has many unanswered problems. Especially, the geochemistry of iodine has been found interesting and complicated. Knowledge about the minor chemical forms of the halides in the marine environment is extremely desirable in order to understand better the distribution of halogens in the air, sea water and sediments. The work this laboratory has carried on (Duce, Winchester, 1963, 1965) urged the necessity of pursuing the study of organic halogen compounds in the ocean water. Also it is hoped that by measuring the organic halogen compounds, some light can be thrown on the iodide-iodate distribution problems in sea water.

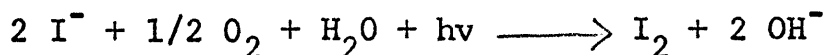
(1) Organic halogen compounds and air-sea halogen relationships.

As a well-known and interesting fact, the iodine to chlorine ratio is considerably higher in the air, in rain, and in aerosol particles of marine origin. The content of iodine is also higher in air masses from the ocean than those from inland (Goldschmidt, Rankama and Sahama, 1946; Duce et al., 1963). To explain this phenomenon, either a physical chemical mechanism for the escape of iodine into the atmosphere or a mechanical mechanism of enriched iodine spray, or both in combination, must be supposed. Some thought that

iodine was formed by oxidation of iodide at sea surface and the free iodine then escaped to the air due to its high volatility. It has been suggested that the dissolved oxygen in sea water was responsible for the following oxidation:



However, thermodynamic calculations using pH 8.3 for sea water and the dissolved oxygen concentration as 0.442 millimoles/l. at 25°C and 19‰ chlorinity, indicated that the resulting equilibrium concentration of I₂ would only be 10⁻²⁵ mole/liter. Photochemical oxidation is another possibility. The chemical reaction being,



since the iodide ion in aqueous solution has a rather strong absorption band in the wave-length range 350 mμ to 230 mμ. Miyake and Tsunogai (1953) used radioactive iodine¹³¹ and showed the release of free iodine into the air in the presence of ultraviolet light, and this certainly indicated strongly that photochemical oxidation of iodide is a possible mechanism for the escape of iodine into the air. By integrating the average evaporation rate and solar radiation, they estimated the total evaporation rate as 4x10¹¹ g/yr. which is close to the annual precipitation rate of 5x10¹¹/yr. Some believed organic iodine compounds also play an important role in this enrichment of iodine in oceanic atmosphere. Loir and Legangneus (1925) stated that the iodine in sea air is mostly in the organic

form, and that iodine in subsurface water exists as inorganic iodine, but on the sea surface, it is present in an organic film and the iodine rich sea air is the result of release by spores and debris of abundant sea weeds and algae. Aside from this active liberation of iodine by a biological mechanism, Blanchard and Woodcock (1957) reported that the aerosol nuclei which originated from the breaking of the sea water bubbles might be more of the composition of the surface film layer rather than the bulk of sea water. Kientzler (1954) found that the most effective way to clean a surface from an organic film was to blow air through and remove the injected bubbles. Blanchard (1955) measured the surface tension change before and after small bubbles had been allowed to bubble through water with an oleic acid film and showed that the film mechanism was transferred to the aerosol. This proves the bubble is an efficient way of removing organic components in the solution. A natural occurrence of this film-removing mechanism was suggested by Woodcock (1948) in his work with "red tide." Dean held the opinion that most of the iodine in New Zealand rain water were derived from disintegrated algae and planktons of ocean spray. The high degree of enrichment of organic phosphorous and nitrogen in rain was also suggested as an evidence of this biologically responsible enrichment mechanism. A rather clear indication can be seen from the following data, Dean, 1964 (unpublished):

	Cl ppm	Br ppm	Inorg. I	Total I	% inorg.
surface sea water	18.3	62	54 µg/l.	54	100
massive spray	18.9	63	56 "	64	88
fresh foam	18.9	61	64 "	293	22

The organic iodine excess in the breaking bubble particles was calculated as to be sufficient to account for that in the rain.

A preliminary experiment done by one of our fellow students MacIntyre (unpublished) in studying the increase in the I/Cl ratio in the foam formed by drastically bubbling air through sea water also indicated similar results. A 30 fold increase in I/Cl ratio was observed.

In order to be better able to judge the significance of the different mechanisms, a direct way of measuring the actual quantity of organic iodine compounds present in sea water would be the best solution.

(2) Organic iodine compound and the oxidation state of iodine in sea water

As a well known fact, the only thermodynamically stable oxidation form of iodine in sea water environment should be iodate. The following distribution pattern of the different iodine species in sea water conditions was calculated by Walters (unpublished).

Eh 0.800 pH 8

Cl ⁻	1.	Br ⁻	1.	I ⁻	0.0
Cl ₂	0.593x10 ⁻²⁰	Br ₂	0.938x10 ⁻¹³	I ₃ ⁻	0.0
ClO ⁻	0.907x10 ⁻²³	BrO ⁻	0.225x10 ⁻¹⁰	I ₂	0.0
HCl O	0.471x10 ⁻²³	BrO ₃ ⁻	0.115x10 ⁻¹⁹	IO ⁻	0.0
Cl O ₂	0.403x10 ⁻²⁸			IO ₃ ⁻	1.
HCl O ₂	0.189x10 ⁻²⁷			IO ₄ ⁻	0.0
Cl O ₃	0.489x10 ⁻¹⁸				
Cl O ₄ ⁻	0.319x10 ⁻¹⁵				
HCl O ₄					

Yet the reported data on iodine measurements in sea water indicated a considerable amount of iodide along with iodate. Winkler (1916) first reported the value of 0.008 mg/l iodide and 0.041 mg/l iodate in surface sea water. He postulated that the ratio of iodide to iodate would probably increase with depth without perceptible alteration of the total iodine present. In 1957, Sugawara and Terada did an extensive survey of iodide/iodate measurement in western Pacific Ocean water. AgNO₃ solution was used by them to precipitate iodide in sea water and then the iodate in the filtrate was reduced by sodium sulfite and then determined using the same method. Their results was characteristically random and showed no discernible trends with both location and depth. Some typical results of theirs are plotted in Appendix I to show the striking irregu-

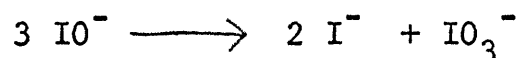
larity. The ubiquitously presented iodide in sea water was again confirmed by Barkley and Thompson (1960). They used an amperometric method to determine the iodate and then determined the total iodine content spectrophotometrically. Their results in the North Pacific and Arctic Ocean is best represented by the following table.

TOTAL IODINE AND IODATE IODINE FOUND IN SEA-WATER
33 SAMPLES (after Barkley and Thompson)

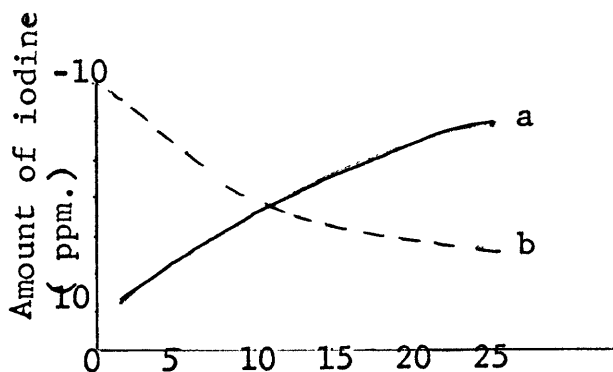
Position	Depth, meters	Chlorinity o/oo	Total Iodine r/Liter	Iodate iodine, r/Liter	Iodate/ iodide
52°06' N, 167°39' W	60	18.10	57	30.2	1.12
	100	18.30	58	25.6	0.79
	200	18.77	68	32.5	0.915
	500	18.94	61	29.7	0.736
	1100	19.07	62	30.3	0.97
48°35' N, 122°51' W	10	15.92	42	20.5	0.95

Yonehara (1965) recently proposed a method for the determination of ultramicro quantities of iodine in the form of both iodide and iodate. The principle used was their catalytic effect on the color fading of ferric thiocyanate. By their method, the sensitivity with maximum error of ± 0.0003 $\mu\text{g}/\text{l}$ was reported and the chloride ion would have no interference at 200 ppm. In their results, randomly distributed iodide/iodate value of a few surface sea water samples were again found.

All these previous informations point to the question of what is the determining factor for the oxidation state of iodine in sea water. Shaw and Cooper (1957) proposed the hypothesis that the oxidized form of iodine in sea water was hypoiodous acid rather than iodate to account for the facts. They assumed that the oxidation of hypoiodous acid to iodate was slow and that the effect of powerful reducing biological material was present. Sugawara and Terada (1958) later questioned the stability of hypoiodous acid and measured the rate of disproportionation for



and proved it to be rather rapid. The reaction rate can be clearly indicated in the following curves



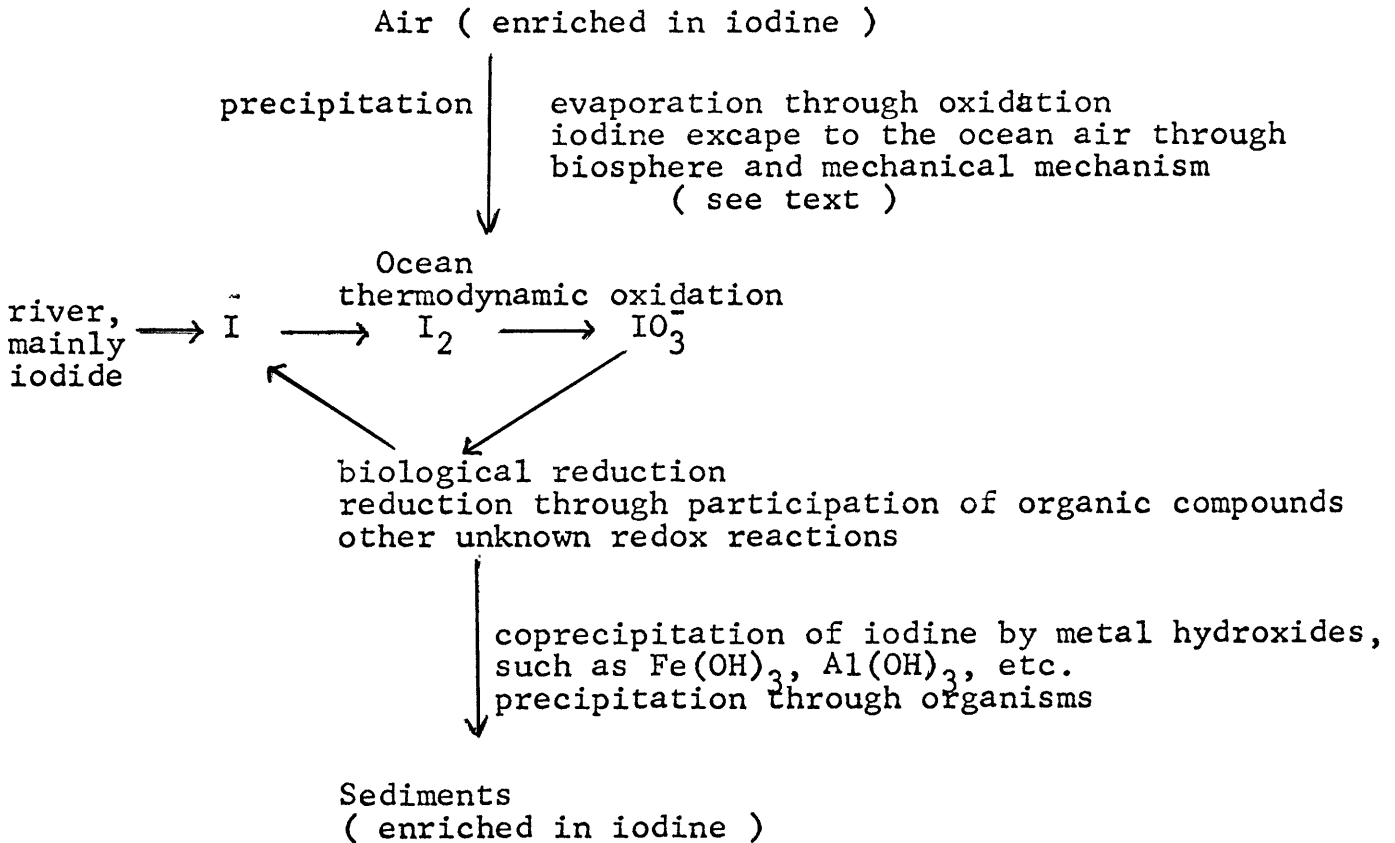
a iodate curve

b hypoiodite curve

and pointed to the unlikelihood of hypiodite ion as the main iodine species in sea water. They attributed the presence of iodide to the extreme slowness of oxidation of iodide to iodate. Johannesson also claimed the oxidized form being iodate from bacteriological evidence. In spite of the evidence and general agreement for iodate to be the oxidized form, the question of what is the controlling factor for the random distribution of iodide/iodate ratio remains unanswered. It could not be explained by the terrestrial contribution of iodide by river water because of the insufficient amount of the latter and also for lack of any geographical correlation. If slow oxidation rate of iodide was the reason, then even the minimum turbulent mixing should be expected to have eliminated the striking differences in the iodide/iodate ratios between neighbouring portions of sea water as have been cited. As Goldberg (1963) pointed out, the marine biosphere which was so intimately involved in the iodine cycle, must have some significance in giving rise to the existence and maintenance of the reduced form of iodine. The interaction between biosphere and iodine in sea will be discussed in the next section. Also, it is conceivably possible that organic compounds in the ocean which are highly reducing might be the real cause of this "slowness" of iodide oxidation. Over the past time, the little consideration received for the role of organic halogen compounds in the whole halogen transformation cycle problem undoubtedly has to do with the enormous difficulties in measuring the organic halogen compounds in sea water because of the

low concentrations present as well as the high inorganic contamination.

A schematic drawing showing the possible picture of the iodine cycle can be outlined as follows:



(3) Possible sources of organic halogen compounds

Very interestingly, both the element itself and the first organic iodine compound were recognized first in marine plant even before its discovery as a constituent in the thyroid gland. Vinogradov (1953) reviewed the determinations of iodine in marine organisms. Many organisms were reported to concentrate iodine very efficiently. For instance, Phycophyta would have iodine concentration 30,000 times as much as that in sea water. Seasonal as well as life-cycle variations exist. The most effective iodine scavenging algae can remove iodine from 30 times its own volume hourly. A summary concentration factors for iodine together with phosphorous in marine biosphere is as below (after Krumholz, Goldberg, Borough, 1957).

Element	conc. in s.w. µg/l.	algae	Invert. soft	skeletal	Vertebrate
I	50	10,000	100	50	10
P	70	10,000	10,000	10,000	40,000

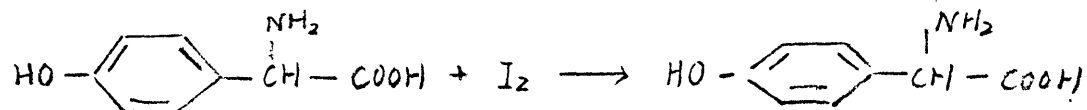
There is disagreement as to what extent the iodine absorbed is transformed into organic form, but it was shown that iodate is not absorbed by algae. The enzyme "iodide oxidase" is responsible for the oxidation of iodide to iodine and I_2 was shown by tracer experiment to be the form which algae absorbs. According to Tong's (1959) study on Nereocystis using I^{131} , after 4 hours of incubation, two thirds of the iodide would be in organically bonded molecules. They also tested the reaction

of non-enzymatic iodination by incubating 0.001 M. hydrogen peroxide with 0.001 M. l-tyrosine dissolved in bicarbonate-Ringer solution and 25% of the added radioactive I^{131} was incorporated into monoiodotyrosine. It is also possible that with the presence of peroxidase type enzyme in the medium, even lower Eh value will be sufficient. In his stability and exchangeability study, Scott (1954) obtained radioactive iodo-compounds after treatment of different tyrosine and thyronine type compounds with I^{131} -iodides.

The presence of organic compounds in sea water has an approximate average of 1 mg C/l. It also has wide concentration variations both horizontally and vertically. Hence if it were the controlling compounds for the iodine oxidation state in sea water, an irregular distribution of iodine forms would be expected. Among the many organic matter investigated, near La Jolla, California, Blaser (1959) found the presence of threonine, as well as uracil, isoleucine, glycine, biotin, purine and tryptophan. He used strains of a mutant bacterium, Serratia marinorubrum, and detected the presence of those compounds by a bioassay method. Koyama and Thompson (1956) identified organic acids of low molecular weight in sea water, such as acetic, oxalic, and glycolic acid in the range of less than 0.1 μ g/liter. Slowery et al. (1959) estimated quantitatively the fatty acids in a vertical profile of sea water. Neuberg et al. (1959) studied the proteinaceous material in sea water.

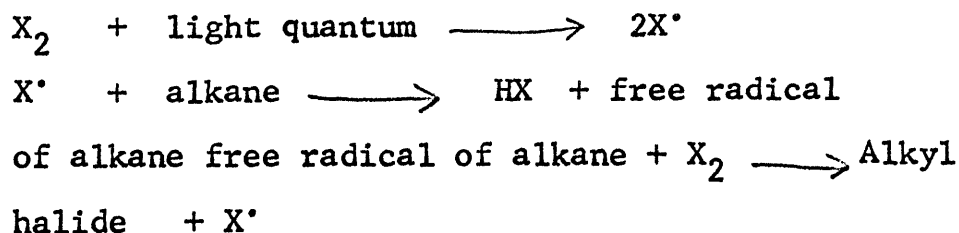
Evidence for proteins in sea water has also been reported by Anderson et al. (1954). Tatsumoto and Hood (1961) used ion exchange analysis and reported a partial quantitative estimation of the amino acids in surface sea water. Among them, tyrosine was estimated to be 3 mg/m^3 . i.e. $3 \times 10^{-6} \text{ g/l} = 2 \times 10^{-8} \text{ mole/l}$. which is $4 \times 10^{-8} \text{ mole/l}$. potentially as diiodotyrosine. This is roughly $\frac{4 \times 10^{-8}}{4.1 \times 10^{-7}} = 10\%$ of the molar

equivalents of iodine in sea water. Since in the laboratory, the iodination of tyrosine can proceed in alkaline solution by just shaking tyrosine with inorganic iodine under ordinary conditions, iodotyrosine type compounds would be able to be formed simply through chemical reactions in sea water. A representative reaction can be written as follows:



Other possible chemical reactions between halogens and organic compounds reactions in sea water are:

1. Substitution of halogen in alkanes: The reaction is homolytic and is catalysed by sun light. The chemical reaction sequences are,



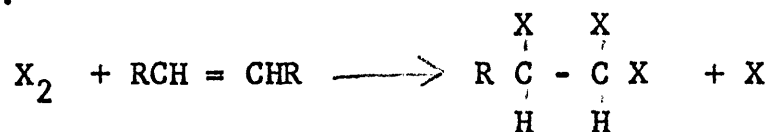
The reaction proceeds slower with iodine and can only be

carried out to a significant extent when HI is continuously removed. Otherwise, HI being a much stronger reducing agent, would cause the back reaction

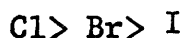


to occur.

2. Addition of halogens on alkenes: The rate of reaction is rather fast and a typical reaction can be written as follows:



Since the addition is via a heterolytic nucleophilic mechanism, the reactivity order is

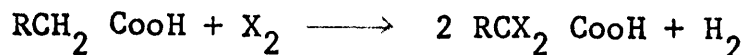


But the addition of hydrogen halide has the reactivity sequence of $\text{HI} > \text{HBr} > \text{HCl}$

3. Reactions with ketones and aldehydes; chlorine, bromine, and iodine substitute readily in ketones having hydrogen on the carbon atom adjacent to the ketonic group. The reaction is catalysed by either H^+ or OH^- ions. The rate of the halogenation reactions has been studied as independent of the concentration of the halogens and that at a given acidity and concentration of ketone is the same for all three halogens.

4. α -halogenation of acids: Because of the electron-withdrawing effect of the carboxylic acid group, the α -hydrogen of the acid is more susceptible to nucleophilic substitution of

halogens. The reaction can be expressed as:



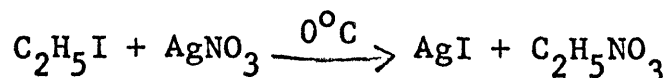
5. Halogenation of macromolecular compounds in sea water: Very little has been studied as to this possibility, yet conceivably, the incorporation of halogens, especially iodine, into macromolecules of such as proteinaceous or cellulose or lipid type compounds should be possible.

The above mentioned reactions all have reasonably fast reaction rates and at extremely dilute environment over long periods of equilibriate time such as that in sea water, They probably could contribute significantly to the determination of halogen form as well as oxidation state in a large scale. Based on the above information, the total disregard of the contribution of organic halogen compounds to the mechanism of air-sea transportation of halogens as well as the iodine form controlling mechanism certainly requires further investigation before it can be taken as justified.

(4) Previous Measurements of Organic halogen compounds.

No conclusive and clear-cut measurement of organic halogen compounds in sea water has been satisfactorily reported yet. Winkler (1916) concluded the absence of organic I compound, but in his method, the procedure for determining both inorganic iodide and organic iodine are by no means non-destructive and the sensitivity in his colorimetric determination seems unable to detect any small amount of organic iodine compounds.

Loir and Legangneux (1925) emphasized the importance of organic iodine both in sea water and in air. The organic combined iodine was separated from inorganic ones by evaporating water to dryness and repeatedly rubbing the residue with 90% alcohol which removed the inorganic fraction away. Sugawara and Terada (1957) reported absence of organic iodine compound in their investigation, but the analytical procedure they used was rather non-specific. They precipitated iodide by silver nitrate in acidic solution and decided the amount of iodide by weighing the precipitate formed. But the reaction condition employed might cause the destruction of the aliphatic halides according to the following reaction:



This reaction can proceed rather smoothly at ordinary temperature; therefore, the determination of inorganic iodide by this gravimetric method can not be a strictly specific one. Furthermore, the scavenging of organic compounds by AgCl flock also may cause great error (see experimental part 2). The ceric-Arsenic catalytic method used by recent investigators is also not entirely discriminative for organic or inorganic iodines. Because this reagent also produces color reactions with organic halogen compounds such as thyroxine and hence is also used as a method in determination of organic iodine compounds. Measurement using this method has been reported by Dean. He attributed the catalytically determined differences before and after chloric acid digestion as the organic iodine and it was reported to be as high as 40% of the

total iodine.

Other worthwhile noticing facts are that the exact form of iodine in air is still not well understood. Erickson (1959) and Bolin (1959) concluded from the plant-atmosphere interchange experiments that most of the iodine in air was in organic form. Also Gulyayeva and Itkina (1962) found enrichment of iodine and bromine in some organic-rich sediments.

(II) Experiment

(1) Introduction

Neutron activation analysis is one of the most sensitive ways of analysing halogen compounds. The sensitivity limit for the different halogens are as follows:

*Sensitivity limit here is defined as the amount of element which would give rise to 10 disintegrations per second after being irradiated in a neutron flux of 10^{13} neutron/cm². sec. for 20 minutes. The cross section data was taken from G. E. Chart of the nuclides, 6th edition, 1962.

Element	Sensitivity (in nanograms)
Cl	1.4
Br	0.058
I	0.077

Previous work in this laboratory gave good precision and proved the chemical procedure reasonably easy to do. The disadvantage of this method is its being non-specific for

organic or inorganic forms. With this in mind, attempts were made to develop a pre-irradiation procedure for separating the inorganic and organic halogens and then use the facilities available to determine the amount of organic halogens by neutron activation analysis.

(1) Coprecipitation with ferric hydroxide

Jeffrey and Hood (1958), Park et al. (1962), Tatsumoto et al. (1961) reported the effective coprecipitation of organic material in sea water by ferric hydroxide precipitate. Recovery of 52-95% of the soluble organic matter on $\text{Fe}(\text{OH})_3$ and a concentrating factor of 10^4 was reported on a single ferric hydroxide precipitation. Usually, the presence of ferric hydroxide is a serious interference in the subsequent determination of organic compound, But neutron activation analysis has the advantage of not being much interfered by the presence of Fe^{+++} , since it would only produce very little activity in comparison with the halogen activities interested, because of the relatively small abundance (0.33% for Fe^{58}) and long half life (45 days) of the important parent and daughter isotopes. Cl^{36} , Br^{82} , Iodide - I^{131} , and Thyroxine- I^{131} tracers were used to determine their efficiency of coprecipitation with ferric hydroxide. In each experiment, 0.232 g. NaCl was added in 5 ml. demineralized water 50λ 5×10^{-6} g/ml. iodide solution was added to make it about the sea water concentration. The bromine tracer had a carrier concentration of 3.0 mg/ml. and no further adjustment was made. Usually 10^4 - 10^5 cpm

tracer was used. 1 mg. $\text{Fe}(\text{NO}_3)_3$ was then added followed by 1 drop of 6 N NH_4OH . After standing for about 20 minutes, the ferric hydroxide was filtered through a 0.45 μ millipore filter and washed with demineralized water. The efficiency for coprecipitation was calculated as:

$$E_1 = \frac{\text{cpm on ferric hydroxide}}{\text{total activity used}}$$

For determining the second or third coprecipitation coefficient, the $\text{Fe}(\text{OH})_3$ was dissolved in 2 ml. 1.5 N. HNO_3 and diluted to 5 ml and then brought to alkaline condition by NH_4OH again.

$$E_2 = \frac{\text{activity in cpm on second ppt.}}{\text{activity in cpm on first ppt.}}$$

The E' (s) are the coprecipitation coefficients obtained by precipitating ferric hydroxide from the filtrate.

The results are summarized in the following table:

TABLE I COPRECIPITATION COEFFICIENT FOR DIFFERENT HALIDES

Species	E_1	E_1	E_2	E_1^{2*}	Remarks
Cl ⁻		8×10^{-5}			from sea water
"		8×10^{-5}			"
"		4.5×10^{-5}			from artificial s.w.
"		3.1×10^{-4}			"
"		5×10^{-4}	10%		"
Br ⁻		1.7×10^{-3}			"
"		1×10^{-3}	6%		"
"		1×10^{-3}	52% (?)		"
"		2.2×10^{-3}			"
"		4×10^{-3}	4%		"
I ⁻		4×10^{-3}		6.9×10^{-3}	"
"		1.3×10^{-2}			"
"		1.5×10^{-3}	41%		"
"		8.5×10^{-3}	28%		"
"		1.6×10^{-3}	33%		"
IO ₃ ⁻		5.6×10^{-3}			"
"		6.4×10^{-3}			"
I ⁻		6.9×10^{-3}	31%		"
"		3.4×10^{-2}	28%		E ₁ overnight
"		2.4×10^{-2}			"
I ₂		1.25×10^{-1}	60.2%		
Thyroxine -I ¹³¹		8%	64%		
Thyroxine		12%	57%		
"		7%			
"		35%	67%		E ₁ overnight
"		21%			

The following results are obtained by adding 100 mg $\text{Fe}(\text{NO}_3)_3$ to 1000 ml. sea water and then adjusting the pH by 6 N NH_4OH to pH 10-12. The precipitate was collected and washed by filtering through a 0.45μ Millipore filter. The solid sample $\text{Fe}(\text{OH})_3$ was irradiated in M.I.T. reactor for 20 minutes. After irradiation, the solid $\text{Fe}(\text{OH})_3$ was dissolved in concentrated HNO_3 and diluted to 25 ml. The post-irradiation chemical procedure is largely based on that of Duce and Winchester (1963) and hence will not be repeated here. Only minor modification because of the presence of Fe^{+++} was made and a flow chart procedure is included in the appendix II to indicate them.

TABLE II NEUTRON ACTIVATION DATA ON
FERRIC HYDROXIDE COPRECIPITABLE HALOGENS

Times of coprecip.	Cl, $\mu\text{g}/\text{l}$	Br $\mu\text{g}/\text{l}$	I $\mu\text{g}/\text{l}$	Br/Cl	I/Cl
3	10 \pm 0.5	1.05 \pm 0.053	0.875 \pm 0.044	0.105	0.0875
2	24.8 \pm 1.2	0.71 \pm 0.036	0.905 \pm 0.045	0.029	0.037
6	34.7 \pm 1.8	0.946 \pm 0.048	0.94 \pm 0.047	0.027	0.027
6	20 \pm 1.0	0.487 \pm 0.025	0.405 \pm 0.020	0.024	0.02
4	22.3 \pm 1.1	1.14 \pm 0.057	0.03 \pm 0.0015	0.051	0.00134
Blank 3 times	16. \pm 0.80	0.038 \pm 0.0019	0.03 \pm 0.0015	0.0024	0.002

* Concentration accuracy= $\pm 5\%$

Confidence level= 67%

Ratio accuracy= $\pm 7\%$

Confidence level= 67%

While the Br/Cl and I/Cl values in sea water are 0.0035 and 2.7×10^{-6} respectively.

From Table I, taking the average E_1 for thyroxine and average E_1 for iodide and iodate (assuming negligible amount of I_2 present in sea water, see calculation above in part I) a separation factor of

$$\frac{9 \times 10^{-2}}{6.6 \times 10^{-3}} = 13$$

is obtained. By using the average coprecipitation coefficients for:

Inorganic Iodine	$E_1 = 6.7 \times 10^{-3}$		
	$E_2 = 0.4$	$E_3 = 1$	(See discussion)
Organic Iodine	$E_1 = 9 \times 10^{-2}$		
	$E_2 = 0.6$	$E_3 = 1$	

Coprecipitated total iodine (average) = 0.78 $\mu\text{g}/1$

Background from 100 mg $\text{Fe}(\text{OH})_3 = 0.03 \mu\text{g}$.

Assuming that the total iodine in sea water was 50 μg . Then we can calculate the fraction of organic iodine, x%.

$$50 \times 6.7 \times 10^{-3} \times 0.4(1-x\%) + 0.6 \times 9 \times 10^{-2} \times 50 \times \frac{x}{100} = 0.78 - 0.03$$

$$x = 24$$

If we use the average $E_1 = 0.5$ for total organic compounds. (After Hood and Tatsumoto) which should be a closer estimation since unfiltered s.w. was treated here. The same calculation leads to:

$$50 \times 6.7 \times 10^{-3} \times 0.4(1-x\%) + 0.6 \times 0.5 \times 50 \times \frac{x}{100} = 0.78 - 0.03$$

$$x = 4$$

Using the same supposition, the total bromine content in sea water being 0.066g., the organic Br. fraction can be calculated

as follows:

$$0.066 \times 2 \times 10^{-3} \times 0.1 \times (1-x\%) + 0.6 \times 0.5 \times 0.066 \times x\% = 6.7 \times 10^{-7}$$
$$x = 3 \times 10^{-3}$$

Since the chlorine value obtained was through a large correction factor from iodine and bromine activity, and also the background was rather high, the calculation of organic chlorine fraction probably would not have too much significance. However, the value $x = 1.2 \times 10^{-4}$ was obtained through the same calculation.

Obviously, these calculations are only a very rough estimation and probably should only be served as a qualitative rather than a quantitative estimation. However, it does indicate that of the three organic halogen compounds, organic iodine compounds are probably the only kind which contribute to a significant fraction of the halogen.

(2) Silver nitrate precipitation

Some silver chloride scavenging experiments were carried out. The consistent bringing down of a considerable fraction of Thyroxine - I^{131} indicated that this method was not suitable for applying to the separation of organic halogen compounds. The results are summarized in the following table.

TABLE III SCAVENGING OF ORGANIC
HALIDES BY SILVER CHLORIDE

Chemical yield measured by weighing AgCl	Percentage thyroxine scavenged by AgCl
92.4%	19.3%
99.7%	49%
92.3%	32.5%

(3) Activated Charcoal Adsorption

Different amount of charcoal was put into 1 liter of synthetic sea water containing either iodide-I¹³¹ or Thyroxine-I¹³¹.

The solution was let stand for 30 min. and then filtered through a 0.45 μ millipore filter. To wash the charcoal, it was redispersed in 500 ml. demineralized water and then refiltered. The activity on the charcoal was counted and the adsorption coefficient was calculated as:

$$E = \frac{\text{Activity on charcoal}}{\text{initial total activity}} = \text{Adsorption coef.}$$

10 ml. of 5×10^{-6} g/l. iodide solution was added to each liter of water.

TABLE IV. ACTIVATED CHARCOAL ADSORPTIVITY
OF IODIDE AND THYROXINE

Species	Amnt. Charc. used	Description	E
I ⁻	60 mg	not washed	4.1%
		washed	2%
I ⁻	120 mg	washed	22%
		washed & dried*	18.3%
Thyroxine-I ¹³¹	120 mg	washed	99.6%
		washed & dried*	99.3%
Thyroxine-I ¹³¹	60 mg	washed & dried*	94.1%

* For drying the charcoal, it was put in a vacuum decicator.

Gentle heating was applied at approximately 60°C. The volatility

loss of inorganic-I is rather high (22% to 18.3%).

From the above results, it could be seen that activated charcoal was able to concentrate efficiently the organic halogen compound and hence rendered them into a more convenient form to be handled. Suitable procedure was searched for further separation of the organic halide from the inorganic ones.

The following tests were made:

- (A) The activated charcoal was packed into a column and the adsorbed organic or inorganic iodine eluted with 500 ml. demineralized water followed by 500 ml. 0.015 N. HNO_3 . The charcoal was then counted.

Species	E	<u>Activity remained on charcoal</u> Original activity on charcoal over-all percentage of halide compounds left on charc.
Thyroxine- I^{131}	61%	94.1% x 61% = 57.5%
Iodide- I^{131}	9.45%	2% x 9.45% = 1.89%

for organic halide v.s. inorg. halide

Enrichment factor = 57.5% / 1.89% = 30

(B) The following experiments were carried out using organic solvents to try to extract out thyroxine. A 50 ml microsoxhlet was used and each time the 60 mg. adsorbed charcoal was extracted with 25 ml. organic solvent at boiling point for 30 min. The organic solvents were then concentrated under reduced pressure to a volume of approximately 2-3 ml.

The results are summarized in below:

$$E = \frac{\text{Activity left in the final 2 ml. organic solvent}}{\text{Original activity on dried charcoal}}$$

= Extraction coefficient

Specied	Solvent	E	Over-all recovery of halides from s.w. in the final 2 ml soln.
I ⁻	Benzene ^{*1}	15%	2% x 15% = 0.3%
I ⁻	"	20% ^{*2}	2% x 20% = 0.4%
Thyroxine	"	43.5%	94.1% x 43.5% = 41%
I ⁻	15 ml. C ₆ H ₆ + 10 ml. Ethyl acetate	22.7%	2% x 22.7% = 0.45%
Thyroxine	"	63.2%	94.1% x 63.2% = 59.5%

*1 The benzene used was purified by extracting the reagent grade benzene twice with drierite and then distilled at its b.p. 80.3°C.

*2 Of the 20% and 15% inorganic iodine extracted, about 1/3 of them were found to be very volatile and was in the organic distillate portion in the concentrating step.

The separation factor through this adsorption-extraction process would be:

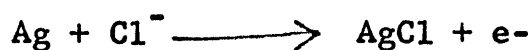
$$\begin{aligned} \text{Using Benzene} \quad c &= \frac{41}{0.4} = 100 \\ \text{Using Benzene + ethyl acetate} \quad c &= \frac{59.5}{0.45} = 132 \end{aligned}$$

Taking a conservative estimation of less than 1% iodine in sea water present as organic iodine compounds, with the above separation factor, inorganic iodine would still give rise to almost 50% of the total activity in the subsequent neutron

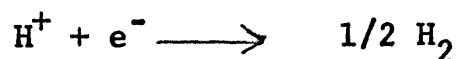
activation analysis. A separation factor of 10^3 is desired in order to reduce the interfering inorganic activity down to less than 10% of the total halide activity produced.

(4) Electrolysis using silver electrodes

If electrolysis using silver anode and platinum cathode is carried out in a solution containing I^- and Cl^- , the anode reaction would be



and the cathode reaction would be



Since $(Ag^+) (I^-) = 8.5 \times 10^{-17}$, so that

Theoretically, we could bring the (I^-) down to less than 10^{-15} mole in the system. Experiments were carried out using the following set-up: A silver plate with surface area approximately 2 cm^2 was used as an anode. A platinum wire connected to a calomel electrode was used as cathode. Different voltages were used and direct current were passed through a 10 ml. sample cell. The solution contained $0.99 \times 10^{-3} \text{ g. } Cl^-$, $5 \times 10^{-6} \text{ g. } I^-$, and I^{131} or Thyroxine- I^{131} . Successive aliquots were taken and counted to determine the iodide or thyroxine concentration still left in the solution. The following results were obtained. The percentage remaining in the solution was calculated as:

$$R = \frac{\text{Activity left in the electrolysis soln.}}{\text{Activity originally in the soln.}}$$

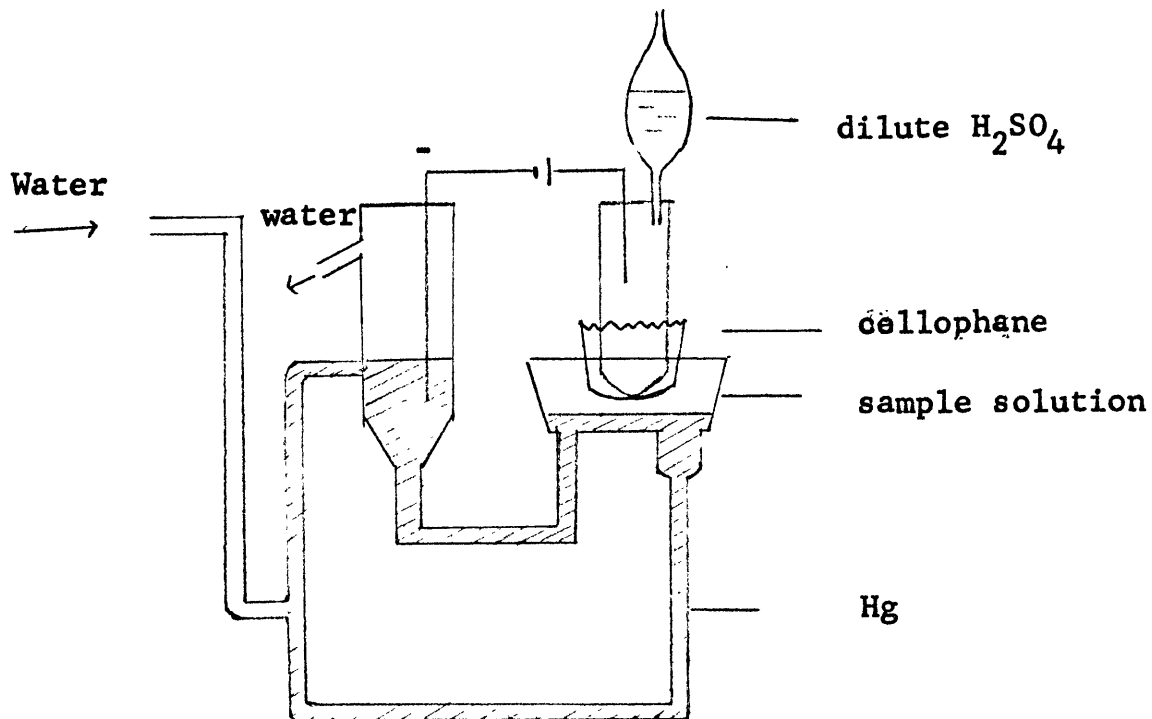
Species	Voltage used	time of electrolysis	R
I ⁻¹³¹	1.5v.	30 min.	74.2%
Thyroxine-I ¹³¹ *	"	"	98.67%
I ⁻	6v.	10 min.	11.1%
		3 hr. 10 min.	2.2%
		6 hr.	1.07%
		10 hr.	1.3x10 ⁻³
Thyroxine	6v.	2 hr.	42%
		5 hr.	19.5%
"	300-600 mv.	6 days	5.8%
I ⁻	"	4 hr.	35%
		8 hr.	3.2%
		28 hr.	2%

* In the case of determining thyroxine removed, 0.01 mg tyrosine was added as a supporting compound. At the optimum condition among the above few trials, at 6v. after 5 hrs., a separation factor of $\frac{19.5}{1.5} = 13$ can be expected. Combining the activated charcoal adsorption, benzene plus ethyl acetate extraction, and the electrolysis, a separation factor of more than $732 \times 13 = 1.7 \times 10^3$ can be obtained. Further investigations seem to be worthwhile to enable better recovery of organic fraction using this principle. Smaller current as well as lower voltage applied in the system might be more suitable.

(4) Electrodialysis

Martin (1947) reported a method of electrodialysis for

separating organic compounds and with salts. More than 90% recovery for most amino acids including glutamic acid and glycine, and more than 98% recovery for average organic compounds were reported. The membrane for dialysis that he used was cellophane membrane. Attempts were made by the author using a Fisher electric desalter which is essentially based on Martin's principle in further separating the inorganic and organic halogen compounds. The principal set-up can be shown in the following diagram.



principle and diagram for electro-dialysis

6 ml of concentrated sulfuric acid in 1 liter of distilled water was used as the anode circulating electrolyte. The circulating mercury cathode was continuously washed with tap water at a flow rate of 300 ml./min. The dialyzing membrane used was Fisher cellulose dialyzing membrane and the testing solution used contained 5×10^{-6} g. I^- , 10^{-5} g. Cl, 10^{-2} mg. tyrosine supporting compound and tracer iodide as well as Thyroxine- I^{131} in a volume of 10 ml. The following results were obtained.

$$E = \text{recovery coefficient} = \frac{\text{activity left in the solution}}{\text{activity originally present in soln.}}$$

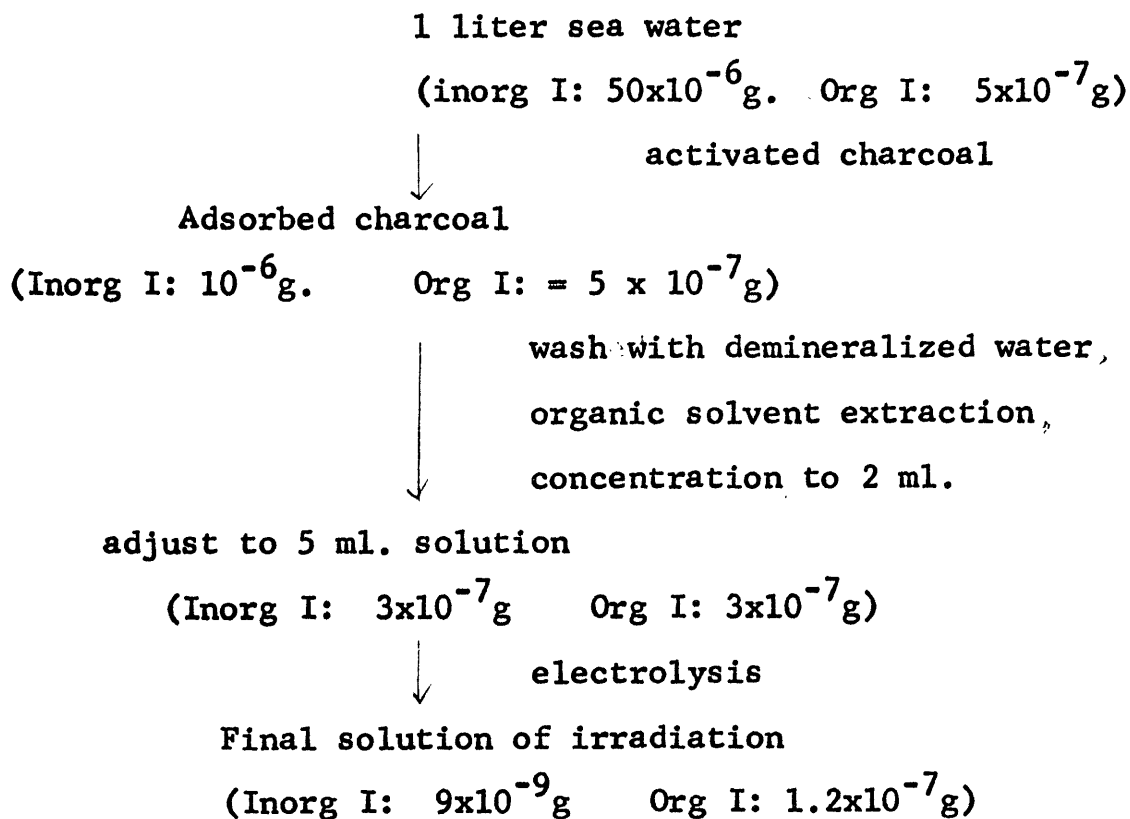
Species	time of elec. dialyzing	current change	E
I^-	10 min.	0.6 - 0.2 amp.	3%
I^-	25 min.	0.2 - 0.14 amp.	1.5%
Thyroxine-I	10 min.	0.6 - 0.2 amp.	16%

The separation factor between organic compound and inorganic compound thus obtained was approximately $\frac{16}{3} = 5$ and was less than that obtained using direct silver electrode. But organic halogen compounds of less polarity than tyrosine and thyroxine would certainly have better recovery rate.

(6) Conclusion

An outline of the tentative procedure can be indicated in the following schematic diagram. By assuming the organic iodine fraction to be 1%, the calculated concentration is

put under each step.



(7) Discussion

1. Non-ionic properties of iodine at extremely low concentration: Chamberlain and Wiffen (1950), Chamberlain (1958), stated that when the amount of carrier is small, I^{131} vapor exhibited peculiar properties and was readily adsorbed on a wide variety of surfaces. May made experiments and calculated that the maximum adsorption on a clean copper surface was about $0.4 \mu\text{g}$. iodine per cm^2 . which was equivalent to a monomolecular layer of molecula of 4A° diameter. In this study, complementary results were obtained; both the ferric hydroxide coprecipitation and the activated charcoal adsorption experiments indicated the likely presence of I_2 as a component when the concentration was very low. The large surface are used in the precipitation might be the cause for this formation of I_2 which appeared to be responsible for the large

adsorptivity and high volatility it showed in the subsequent steps. Sugawara and Terada (1957) suggested that coprecipitation of iodide by metal hydroxides in water to be one possible mechanism for the removal of iodide ions selectively from the environment water and our present data in this study seem to support the view.

2. Comparison of silver electrode electrolysis and electro-dialysis: From the experiments carried out here, high recovery of organic polar compounds such as amino acids could not be obtained by electro-dialysis as reported by Martin. Yet the method itself has the advantage of being able to remove most other inorganic ions at the same time and thus gave a lower background counting in the subsequent neutron activation analysis. Another advantage was that the interfering ions were actually taken away from the sample solution, so that after this step, the samples could be directly irradiated without going through further procedures such as filtration, etc. Electrolysis applying silver electrode is an unlimited method theoretically, yet the disadvantage comes from the fact that silver halide precipitate would be in the system and requires further removal.

3. Comparison of the present outlined procedures for the determination of organically bound halogens with other possible methods: Among the other possible methods in measuring organically bonded halogens. Owing to the low concentration

of organic halides, only the following two methods seem to be potentially useful.

- a. Gas chromatography using an electron detection device.
- b. Paper chromatography using internal tracer to spot the compound positions and then followed by neutron activation analysis.

Yet the problem and difficulties would arise since a much more exact knowledge which is now lacking as to what are the organic compounds present would be very critical in applying these methods. Also, the fact that the organic halogens present might be in many different forms and therefore the sensitivity limit required for detection would be even higher and this might be the limiting factors in the chromatographic methods approach.

(18) Suggestions for application of the determination of organic halogen compounds.

By measuring the separate quantities of iodide, iodate, and organic iodine compounds respectively on sets of sample sea water with difference in biological activities, significant information probably can be expected to help evaluating the contribution of biological activity to the iodide-iodate ratio. By measuring the organic iodine content of the surface sea water, a better evaluation of the organic contribution to the atmospheric iodine enrichment should be possible.

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APPENDIX I

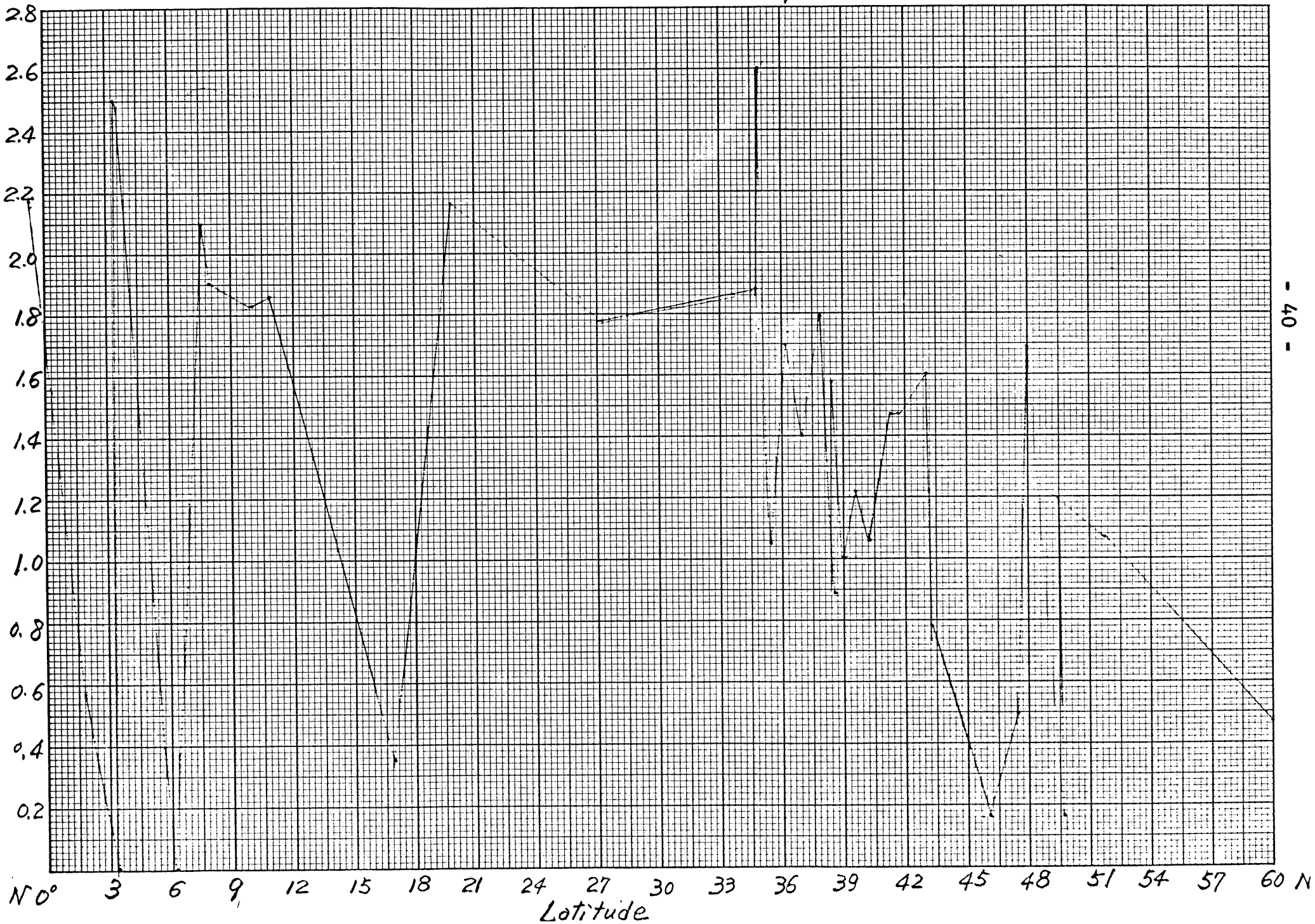
DISTRIBUTION OF IODATE/IODIDE IN SEA WATER:

IT'S CHARACTERISTIC RANDOMNESS.

(after Sugawara and Terada)

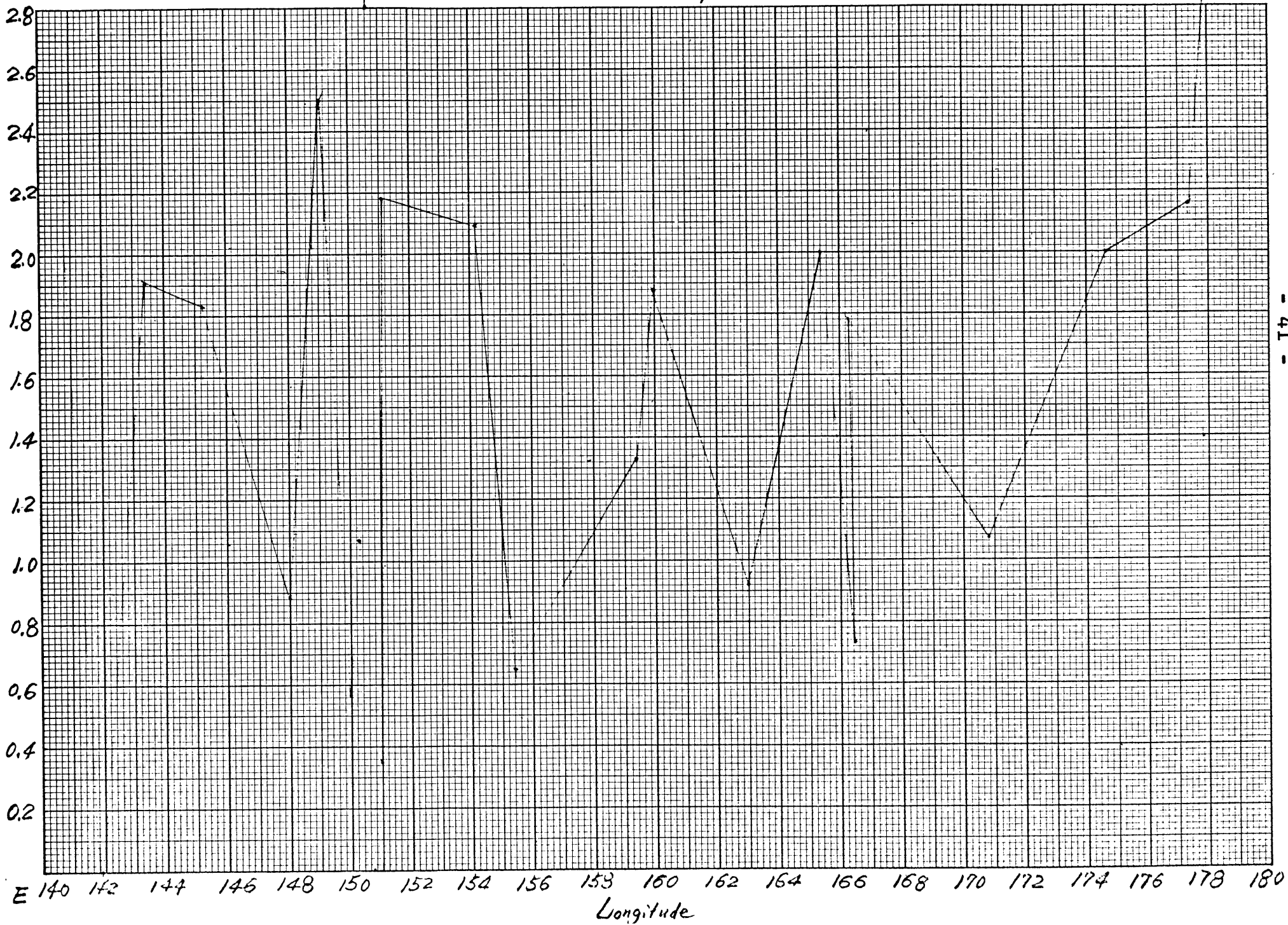
$I_{O_3^-}/I^-$

Depth: 0 m.



$10^5 / I^-$

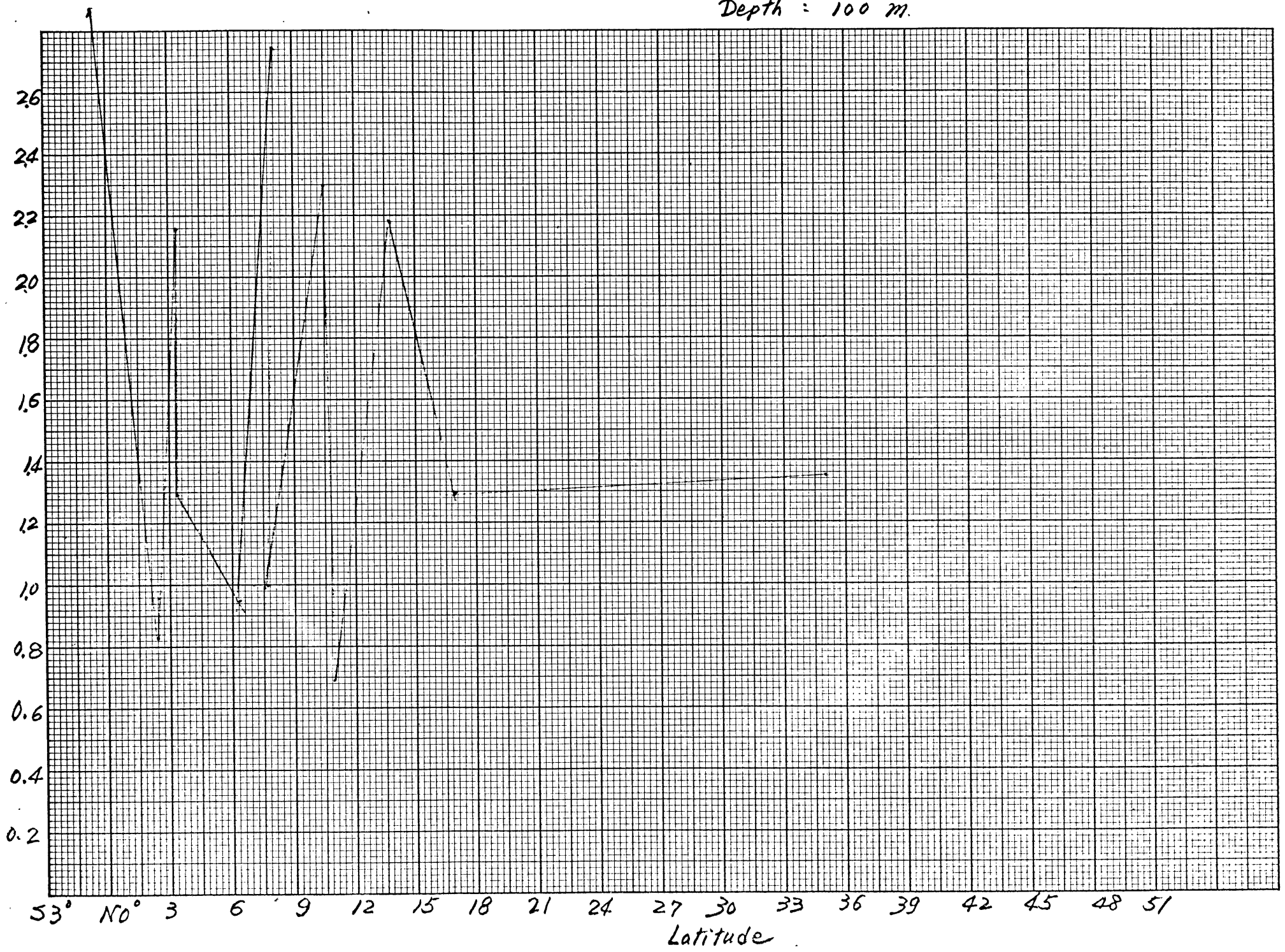
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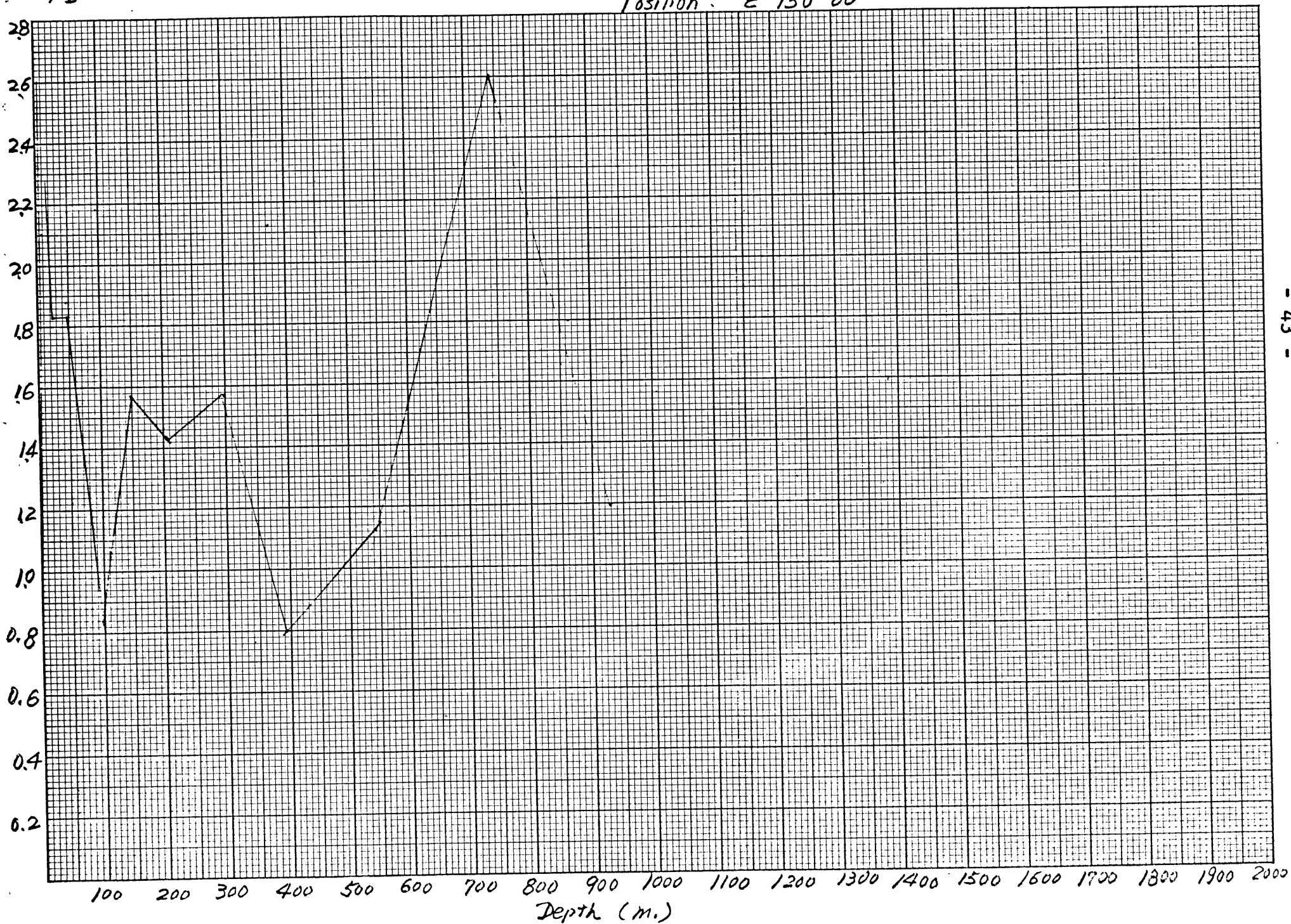
103/I

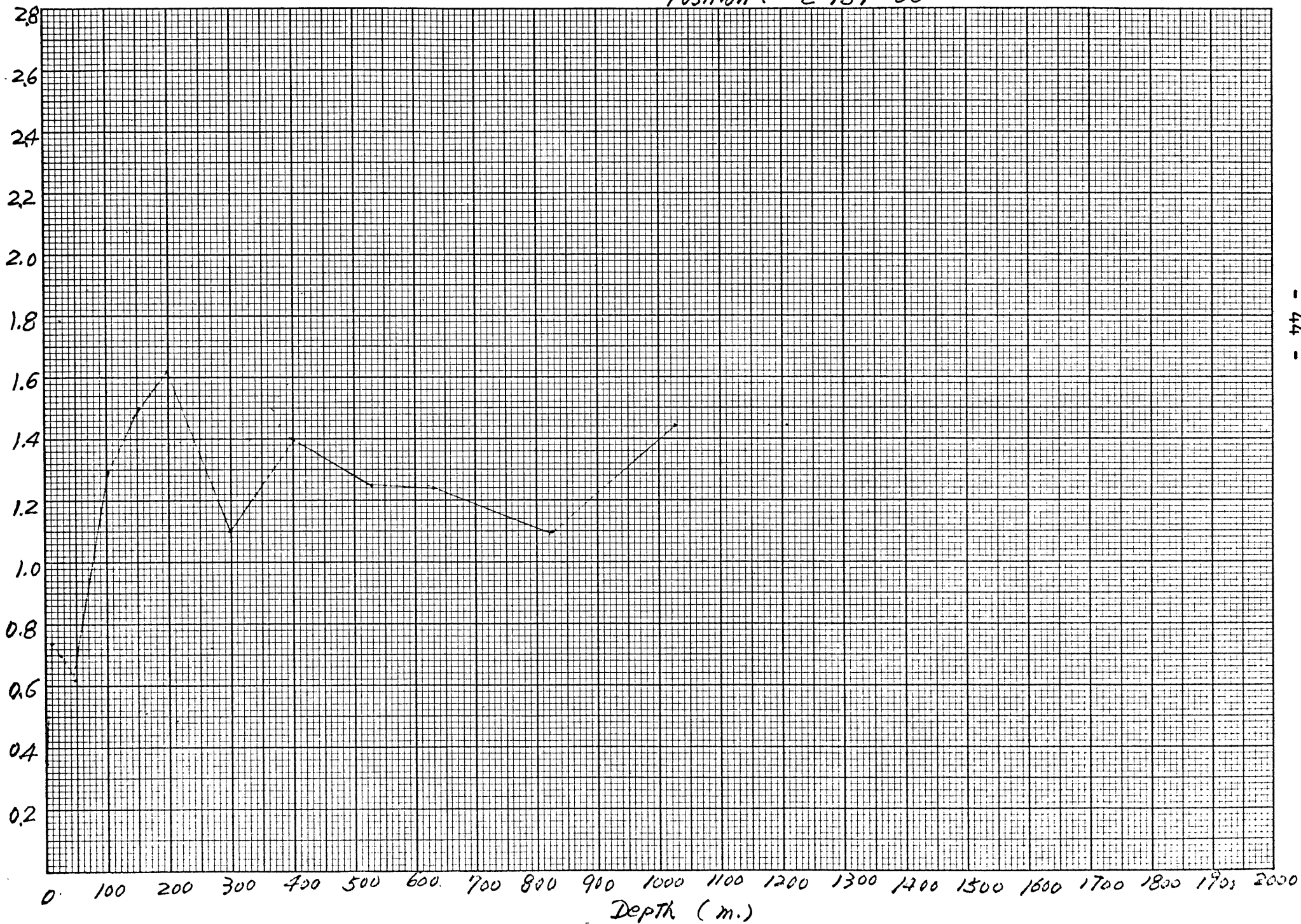
ROFFEL WESSER CO.

Depth : 100 m.



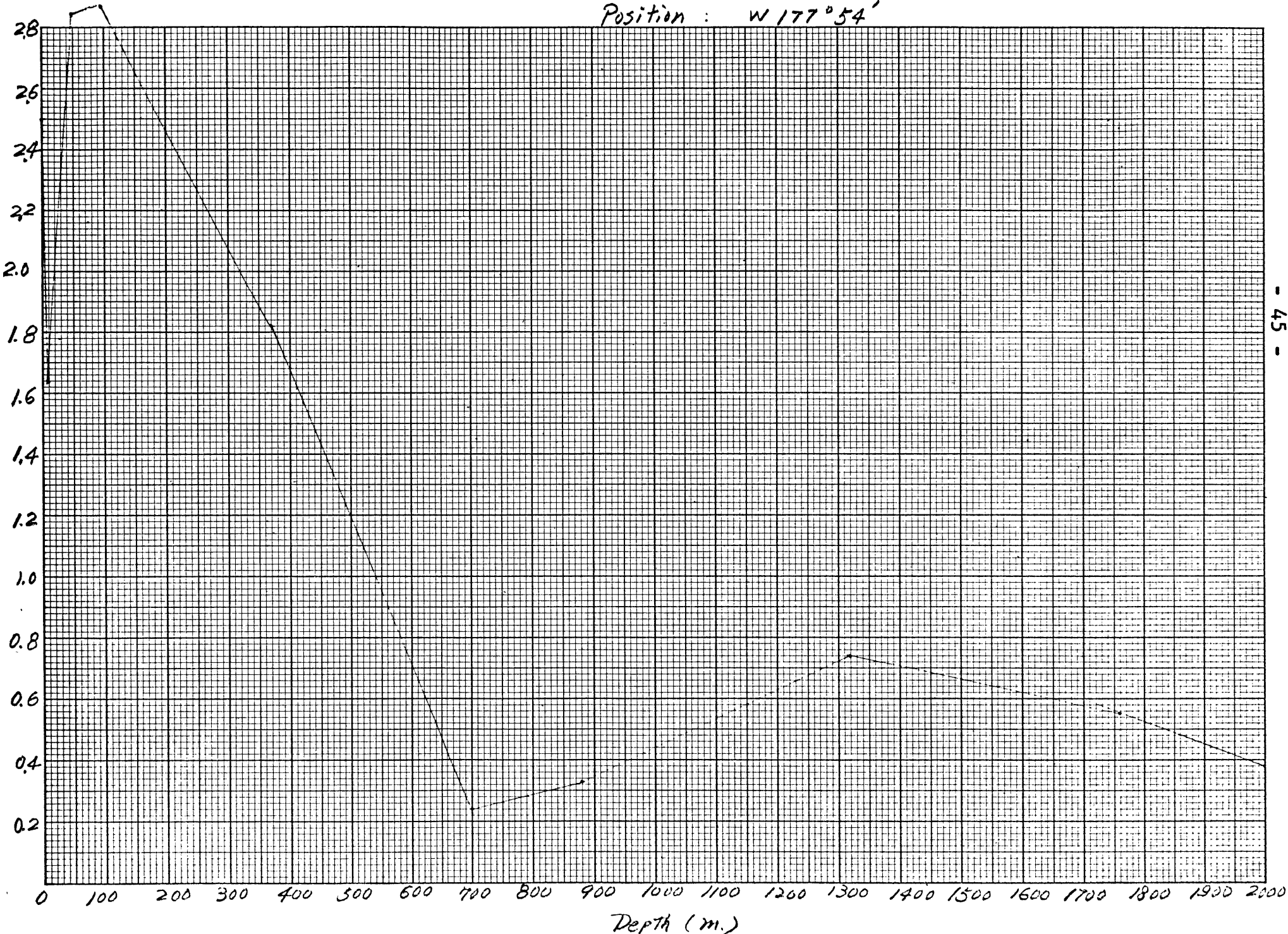
- 42 -

IO_3^-/I^- Position: N 02°13'
E 150°00'

$I_{O_3^-} / I^-$ Position: N 17° 00'
E 151° 00'

IO_3^-/I^-

Position : N 35° 01'
W 177° 54'



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APPENDIX II
FLOW CHART DIAGRAM OF THE POST-IRRADIATION
CHEMICAL PROCEDURES FOR THE
NEUTRON ACTIVATION ANALYSIS
OF HALOGENS

100 mg. $\text{Fe}(\text{OH})_3$ precipitate from sea water
irradiation (20 min.)
dissolve in conc. HNO_3 ,
adjust volume to 25 ml.

