UNIVERSITY of WASHINGTON

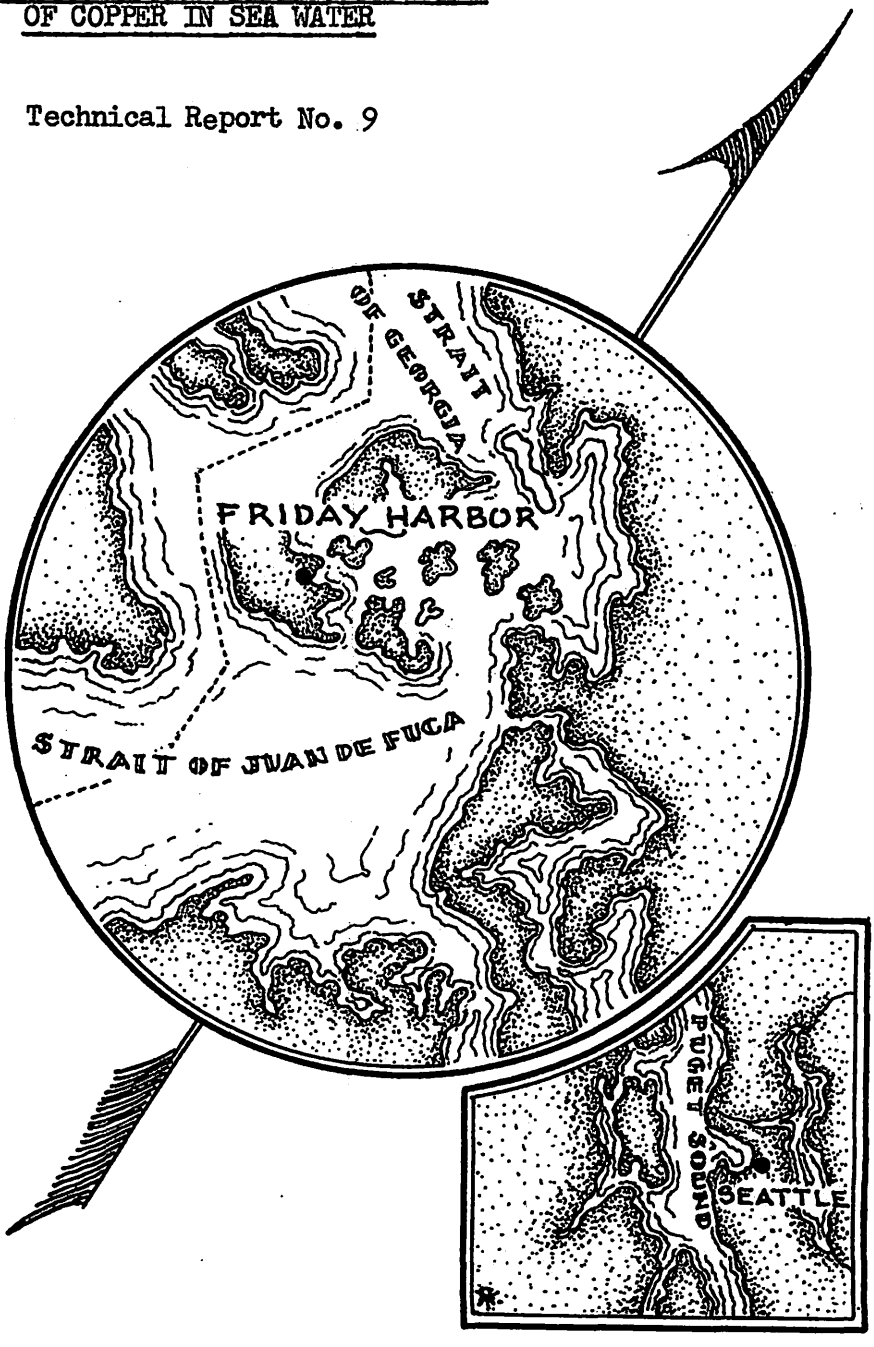
OCEANOGRAPHIC LABORATORIES

THE DETERMINATION AND DISTRIBUTION OF COPPER IN SEA WATER

PART I

THE SPECTROPHOTOMETRIC DETERMINATION
OF COPPER IN SEA WATER

Technical Report No. 9



Office of Naval Research
Contract N8onr-520/III
Project NR 083 012
March, 1952

UNIVERSITY OF WASHINGTON OCEANOGRAPHIC LABORATORIES
Seattle and Friday Harbor, Washington

Reference No. 52-2

THE DETERMINATION AND DISTRIBUTION OF COPPER IN SEA WATER

PART I

THE SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN SEA WATER

by

Tsaihwa J. Chow and Thomas G. Thompson

Technical Report No. 9

Office of Naval Research
Contract N8onr-520/III
Project NR 083 012

March, 1952

Richard H. Fleming
Director

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

THE DETERMINATION AND DISTRIBUTION OF COPPER IN SEA WATER

PART I

THE SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN SEA WATER

ABSTRACT

The spectrophotometric determination of copper in sea water has been studied using sodium diethyldithiocarbamate as the color forming reagent. This reagent, compared with the frequently used dithizone, affords simpler operation, less interference from other metallic ions, higher sensitivity and greater accuracy. Xylene has been found to be most desirable for extracting the copper diethyldithiocarbamate. Factors studied in some detail include the effects of varying the extracting time, concentration as it affects the coefficient of extraction, amount of reagent, hydrogen ion concentration, salinity, concentration of oxidizing and reducing agents, and the stabilities of the diethyldithiocarbamate reagent and the colored copper diethyldithiocarbamate. The composition of the color complex has been determined by the continuous variation method. Methods for minimizing the effects of interfering substances have been discussed. Samples of coastal sea water have been analyzed for copper by this method.

THE DETERMINATION AND DISTRIBUTION OF COPPER IN SEA WATER

PART I

THE SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN SEA WATER

INTRODUCTION

Copper occurs in sea water in an extremely small concentration but, similar to the nutrient salts, it plays an important role for certain marine organisms. Invertebrates, oysters in particular, concentrate copper to a considerable extent. It appears in the blood of some invertebrates in the pigmented respiratory compound, hemocyanin, serving as an oxygen carrier in a role somewhat analogous to that of iron in hemoglobin in the blood of mammals. It is present in the proteins hemocuprein and hepatocuprein in mammalian liver. It occurs in marine plants and appreciable quantities are found in certain enzymes where it performs as an oxidation catalyst.

The lack of a convenient and accurate method for the determination of small amounts of copper has held up a true understanding of its role in the sea, sediments and marine organisms. The primary purpose of this investigation was to develop such a method. The secondary objective was to determine the copper concentration and its variation in the waters of Puget Sound and the San Juan Archipelago, paying attention to season, tide, location and depth, and other physical or biological changes.

DISCUSSION OF LITERATURE

Dieulafait (1879) repeatedly detected copper qualitatively in sea water by means of a spectroscope, the sea water being concentrated by evaporation and the copper precipitated as a sulfide. Hiltner and Wichmann (1919) reported a trace of copper in sea water taken one mile off-shore from West Sayville, New York.

Rose and Bodansky (1920) made sea water ammoniacal and used a colorimetric method to estimate the copper directly as the ammonia complex. Their samples were taken thirty feet from the beach near Galveston, Texas. Severy (1923) used Rose and Bodansky's method to determine the copper content in marine animals but found none in sea water samples taken from the Pacific Ocean near Pescadero Island.

Orton (1923) concentrated sea water by evaporation, acidified the solution, saturated it with hydrogen sulfide and compared it turbidimetrically with similar tubes containing known amounts of copper. His findings for English Channel water are high, 200 micrograms of copper per liter, attributed to contamination from a copper bolt found in the sampling bottle.

Meulen (1931) found copper in the residue obtained from the evaporation of sea water. The copper in this residue was precipitated as sulfide, dissolved in nitric acid and estimated as the copper ammonia complex.

Atkins (1932, 1933) concentrated the copper in sea water by electrolytic deposition on a platinum gauze cathode. The deposited

copper was then dissolved in sulfuric acid, the resulting solution neutralized and the copper estimated colorimetrically as diethyldithiocarbamate. In a later work he extracted the copper diethyldithiocarbamate complex directly from sea water by shaking with chloroform. Identical values were obtained by both methods. His results indicated more copper in the deep water than at the surface.

Prytherch (1934) used the carbamate method to determine copper removed from sea water by precipitation with hydrogen sulfide and subsequent filtration. The highest copper concentration in coastal waters was found during low water periods and attributed to the effect of river discharge. Concentrations increased in the proximity of river mouths indicating river effluent as a source of copper. He studied the role of copper in the setting of oysters and found correlation between the vertical and horizontal distribution of oysters and of dissolved copper in different coastal regions.

Riley (1937) concentrated copper by the extraction method of Atkins employing iso-amyl alcohol instead of chloroform, and compared the color to that of 0.001 normal potassium dichromate solution. Experiments on filtered sea water showed much of the copper associated with the solid particles present in colloidal suspension. He found the greatest concentration of copper in the Gulf of Mexico in low salinity coastal water with some indication of concentrations decreasing seaward. He stated that copper is not a limiting factor in the open ocean to those animals which require it for the synthesis of hemocyanin.

Bardet, et al. (1938) concentrated 60 liters of sea water by

evaporation and found copper among the trace metals detected spectrographically.

Meyer (1938) suggested a variation in the diethyldithiocarbamate procedure to eliminate the initial concentrating of the copper. The samples of sea water were analyzed directly in an acidified solution by means of a Pulfrich photometer.

Kalle and Wattenberg (1938) using Meyer's photometric method determined copper in water from the north Atlantic Ocean and found a high concentration at the bottom. They stated that the copper content could not affect the color of the sea water.

Woodbridge and Thompson (1938) analyzed Puget Sound waters with their modification of Atkins' electrolytic deposition method and reported the lowest copper content in October and the highest in December. The authors questioned their results because of possible contamination from the sampling device.

Noddack and Noddack (1939) using a spectroscopic method determined 21 heavy metals including copper in marine animals and sea water. The metals were concentrated from sea water using hydrogen sulfide. They calculated the concentration factors or extent to which the heavy metals were accumulated by several marine animals, comparing these concentrations to those found in sea water.

Isibasi, et al. (1940) added nickel to sea water, precipitated it along with the copper as the sulfide in an almost neutral solution, dissolved the sulfides in nitric acid, made the solution ammoniacal, and reprecipitated the copper with benzoin oxime in alcoholic solution.

Brown and Thompson (1942) using Meyer's diethyldithiocarbamate and Pulfrich photometer method found no seasonal variation in copper content in Puget Sound and adjacent waters.

Galtsoff (1943) reported his earlier work (1934) on trace metals in sea water describing seasonal fluctuations, physiological roles, and accumulations by marine organisms. For the determination of copper he used Atkins' electrolysis-carbamate method examining the chloroform extract with a Duboscq colorimeter. No systematic fluctuation of copper was found within one-half a period of tidal cycle. Near the river mouths somewhat higher concentrations were found than elsewhere.

Buch (1944) analyzed waters from the Baltic Sea using dithizone as the colorimetric reagent. Copper and other metals were extracted from sea water with dithizone into chloroform at a pH value of 4, the copper and zinc being determined separately by regulating the pH of the solution. Koroleff (1950) studied this method with respect to extraction equilibrium, salt effect, solvents and extraction time.

Barnes and Rothschild (1950) determined the copper content in sea urchin semen and in sea water using the carbamate extraction method with chloroform solvent. The color intensity was measured photometrically and compared with a prepared calibration graph.

Morita (1950) on the basis of an improved dithizone method concluded that the copper content of sea water is probably less than one microgram per liter, and attributed higher values hitherto reported to defective analytical procedure.

In studying trace elements in brown algae and sea water, Black

and Mitchell (1952) using a spectroscopic method found much higher concentrations of copper in sea water than reported by other investigators. Their method of sampling was not given. They also found that no change in the heavy metal concentration ~~was~~ resulted from diatoms adhering to the glassware or from surface adsorption of trace elements on the glass.

Results of the above investigators are summarized in Table I.

TABLE I

COPPER CONTENT OF SEA WATER FOUND BY VARIOUS INVESTIGATORS

Date	Investigators	Source of Water	No. of Samples	Microgram-atom/liter
1879	Diculafait (a)	Mediterranean Sea	1	0.16-0.19
1919	Hiltner and Wichmann (l)	West Sayville, N.Y. and Keyport, N.J.	2	Trace
1920	Rose and Bodansky (b)	Galveston, Texas	1	2.20
1923	Severy (b)	Pacific Ocean		No trace
1923	Orton (h)	English Channel	1	3.15
1931	Meulen (b)	Roscoff (Brittany)	1	0.95
1932	Atkins (d)	English Channel	1	0.16
1933	Atkins (e)	Rivers entering English Channel	6	0-0.60
1933	Galtsoff (d)	Woods Hole, Mass.	9	0.13-0.54
1934	Prytherch (c)	New Haven, Black Rock and Southport Harbors		3.15-9.50
1937	Riley (e)	Gulf of Mexico (surface)	20	0.016-0.24
1938	Bardet, et al. (j)	Roscoff (Brittany)	1	1.42
1938	Meyer (g)	Baltic Sea and North Sea	16	0.095-0.41
1938	Kalle and Wattenberg (g)	North Atlantic (surface)	10	0.047-0.19
		Ditto (great depth)	1 series	0.16-0.47
1938	Woodbridge and Thompson (d)	Puget Sound, Wash. and Bering Sea	70	0.11-0.28
1939	Noddack and Noddack (a)	Zoology Station Kristineberg, Sweden	1	0.063
1939	Galtsoff (e)	Bahamas	6	0.016-0.13
1940	Isibasi, et al. (f)	Japan Sea	1	0.47
1942	Galtsoff (e)	Long Island Sound, N.Y.	18	0-1.50
1942	Brown and Thompson (g)	Friday Harbor, Wash.	60	0.047
1944	Buch (i)	Baltic Sea		0.032-0.13
1950	Barnes and Rothschild (e)	Millport Marine Station, Scotland (surface)	3	0.095
1950	Morita (i)	Tokyo Bay, Japan -	21	0.016-0.095
1952	Black and Mitchell (j)	Plymouth, England	4	0-47.0
1952	Thompson and Chow (k)	Friday Harbor and Seattle, Wash. (surface)	100	0.012-0.030

(a) Spectroscopic
(b) Ammonia colorimetric
(c) Hydrogen sulfide precipitation and carbamate
(d) Electrolysis and carbamate
(e) Extraction as carbamate
(f) Hydrogen sulfide precipitation and benzoin oxime
(g) Direct estimation as carbamate
(h) Turbidimetric
(i) Dithizone colorimetric
(j) Spectrographic
(k) Direct spectrophotometric
(l) Hydrogen sulfide precipitation

CHEMICALS AND EQUIPMENT

All chemicals used in this investigation were analytical grade and tested for traces of copper. The water employed for the solutions and tests was redistilled from an all glass still. In the preparation of all reagents special care was used to avoid contamination.

One per cent (w/v) sodium diethyldithiocarbamate reagent was prepared every few weeks using pure sodium diethyldithiocarbamate (Eastman Kodak Co.), and the reagent solution stored at a pH value of 10.

The sodium chloride solution was prepared by dissolving 30.24 grams of the salt in redistilled water and diluting to one liter. The chlorinity, 18 °/oo, of this solution is approximately equal to that of coastal sea water.

A stock solution containing 10 microgram-atoms of copper per ml. was prepared by dissolving 2.505 grams of analytical grade $CuSO_4 \cdot 5H_2O$ in redistilled water and diluting to one liter. A solution containing 0.25 microgram-atom of copper per ml. was made by forty fold dilution with redistilled water. Other standard metallic ion solutions were prepared by a similar method.

Polyethylene containers were used whenever possible in order to minimize contamination from glassware. The extraction was carried out in polyethylene bottles thoroughly washed with xylene as new bottles sometimes gave an emulsion with xylene during the extraction. A wrist action Burrell mechanical shaker was employed for uniform agitation

during the extraction process. In order to avoid contamination from metal sampling bottles, surface sea water was collected by immersion of a seasoned Pyrex glass bottle and transferred immediately to polythylene storage bottles. The absorbency * (optical density) readings were measured with a Beckman DU spectrophotometer using corex glass cells of 1 cm. optical path.

---

* According to the National Bureau of Standards, Letter Circular LC - 857 (1947).

ANALYTICAL PROCEDURE

On sea water containing much plankton this growth was first removed by filtering through a sintered glass plate to avoid an emulsion with xylene which might otherwise form during the extraction process. In most cases 500 ml. of the original sea water (pH 7.5-9.0) was measured directly into a polyethylene bottle, two ml. of 1% diethyldithiocarbamate reagent added, and the sample extracted with 5 ml. of distilled xylene for one hour using a Burrell shaker. The xylene layer was pipetted by a medicine dropper, transferred to the absorption cell, and the absorbency read in the Beckman DU spectrophotometer at the wave length of 436 mμ using a slit width of 0.05 mm. Distilled xylene was used as a reference.

The copper content of the sea water sample was then obtained using a calibration graph based on known amounts of copper. A corrected absorbency reading of 0.005 was found to correspond to 0.0015 microgram-atom of copper per 500 ml. of sea water. The molar extinction coefficient of copper diethyldithiocarbamate in xylene at this wave length was calculated to be 16,800/cm./mole.

Although this method was developed for determining micro-quantities of copper in sea water, it is believed that the procedure is of general application.

EXPERIMENTAL

Selection of Reagent and Extracting Solvent

Dithizone (diphenylthiocarbazone) has long been considered as a sensitive reagent for copper. It is a violet-black crystalline material which yields characteristic colors with a number of heavy metallic ions. Separation of these colored complexes has been achieved by regulating the pH of the solution to be extracted, adding masking agents that form complexes with interfering ions and varying the extracting solvent.

Since dithizone is a sensitive but not specific reagent, it is difficult to avoid contamination leading to errors in the determination of copper. Zinc is relatively abundant and gives the most difficulty. The reagent itself is very unstable and easily oxidized to form an inactive yellow product. The process involves two colors with uncertain reproducibility. Furthermore, the equilibrium point of the extraction is dependent upon the acidity, and complete extraction ~~could~~ can not be attained at the equilibrium.

Sodium diethyldithiocarbamate was introduced by Delepine (1908) as a reagent for detecting traces of copper. In order to increase the sensitivity of the determination, the colored copper complex is concentrated by extraction. Factors to be considered in the selection of the extracting solvent are its extractibility, solubility in water, volatility and specific gravity. Amyl alcohol, iso-amyl alcohol, iso-amyl acetate, amyl acetate and chloroform are sufficiently soluble in water to give a serious error in the determination because of the large volume of sample required. Carbon tetrachloride and bromobenzene which are less soluble

have been used as extracting agents. Xylene, however, was found by the authors to be much more satisfactory. It is quite insoluble in water, non-polar, comparatively non-volatile and readily separated from water because of its lower specific gravity. The colored copper complex in xylene did not show any change in the maximum absorption wave length.

Optical Absorption Spectrum of Copper Diethyldithiocarbamate

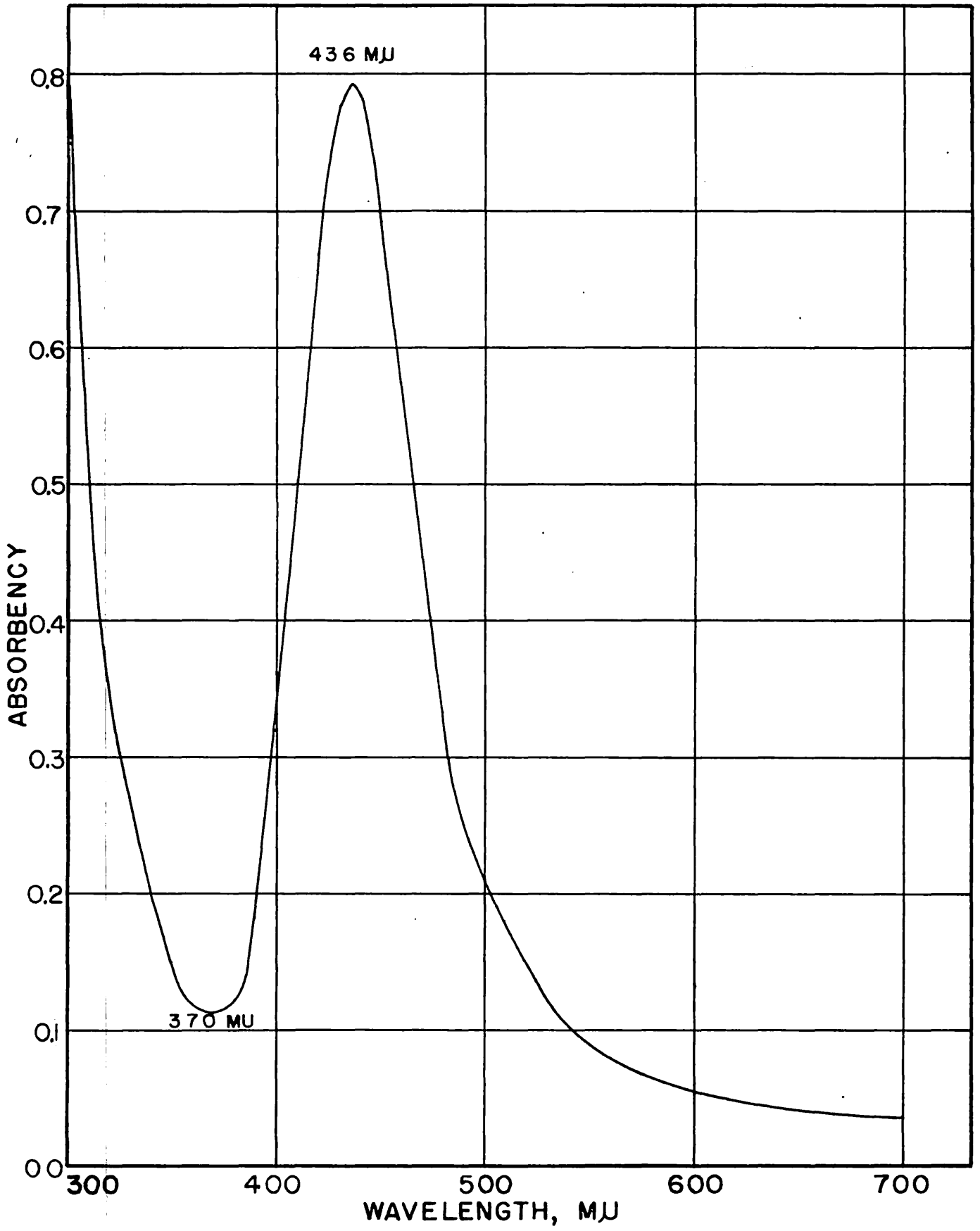
Copper diethyldithiocarbamate was extracted with xylene from solutions containing 0.25 microgram-atom of copper. The solutions had a chlorinity of 18 °/oo and a pH value of 8. The absorbencies of the colored xylene solution were measured at different wave lengths over a range from 300 mμ to 700 mμ and results of which are shown in Figure 1. Maximum absorption was observed in the curve at the wave length of 436 mμ. Absorption decreased sharply when the peak was passed and reached the minimum at 370 mμ. The increased absorption shown toward the ultra-violet region was due to the excess reagent.

The absorption of various copper concentrations at 436 mμ with a 0.05 mm slit width was reproducible and followed Beer's Law. Unless noted absorbency was made at this wave length and slit width throughout the investigation.

Stability of Sodium Diethyldithiocarbamate Reagent

Sodium diethyldithiocarbamate reagent in solution decomposes slowly with the formation of carbon disulfide. Murakami (1950) suggested various methods for stabilizing the reagent by adding chloroform or hydroxylamine on the basis that the instability was due to oxidation and bacterial action. It was observed in this investigation that the pH value

Figure 1: General Absorption Spectrum of Copper Diethyldithiocarbamate in Xylene. 0.25 microgram-atom of copper extracted from pH 8, 18 °/oo Cl solution.


436 MU
370 MU
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
ABSORBENCY
300
400
500
600
700
WAVELENGTH, MU

is the main factor which influences the stability of the reagent.

The stability of the reagent, stored in different hydrogen ion concentrations, was studied during 45 consecutive days of observation. Two ml. of the diethyldithiocarbamate reagent (original concentration 0.5 millimole) were treated with a slight excess of copper in 100 ml. of Cl 18 °/oo solution. The colored complex was extracted by the normal procedure. The rates of decomposition are indicated in Figure 2. The reagent decomposed rapidly if it was stored in solutions of pH less than seven. The stability increased with increase of pH values. At a pH of 10 about 30 per cent of the reagent decomposed in forty-five days.

It is concluded that the decomposition of diethyldithiocarbamate is due chiefly to the hydrogen ion concentration. The reaction is

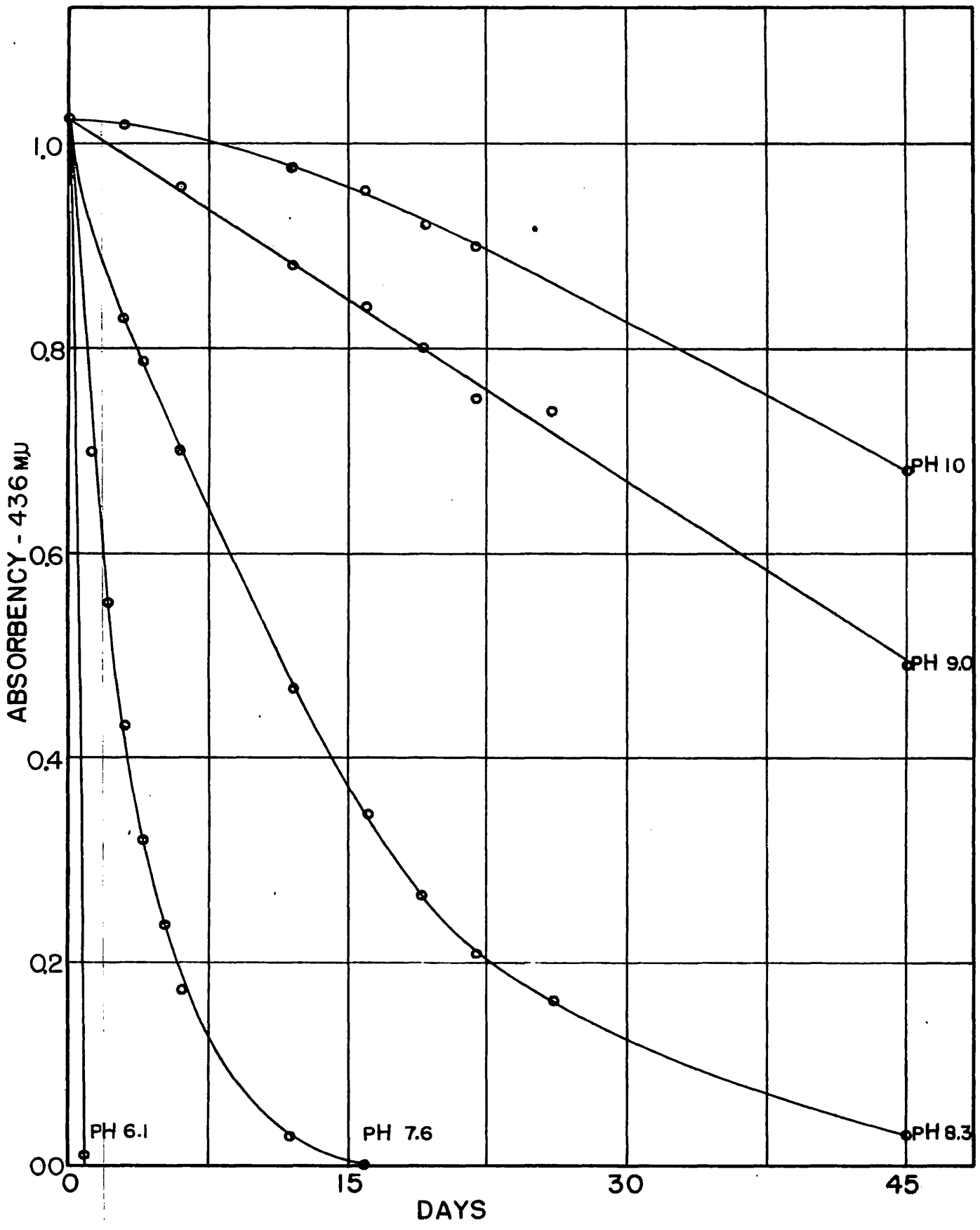
$$(C_2H_5)_2NCSSNa + H^+ \longrightarrow Na^+ + (C_2H_5)_2NH + CS_2.$$

The reagent should be kept slightly alkaline, controlled preferably with ammonium hydroxide.

Stability of Copper Diethyldithiocarbamate

The stability of copper diethyldithiocarbamate in xylene was examined by treating a sample containing 0.25 microgram-atom of copper with diethyldithiocarbamate in slight excess and extracting the colored copper complex with 5 ml. of distilled xylene as described in the procedure. After standing 48 hours in diffused light the absorbency reading showed no change. The color intensity, however, diminished if the solution was exposed to strong light. Fading occurred in absence of excess of the reagent.

Figure 2: Stability of Sodium Diethyldithiocarbamate Reagent. Original concentration 0.5 millimole. Two ml. of diethyldithiocarbamate reagent extracted from 18 °/oo Cl solution at various pH values.


ABSORBENCY - 436 MU
1.0
0.8
0.6
0.4
0.2
0.0
0
15
30
45
DAYS
PH 10
PH 9.0
PH 8.3
PH 7.6
PH 6.1

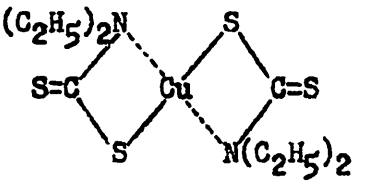
Composition and Structure of Copper Diethyldithiocarbamate

The molar ratio between copper and diethyldithiocarbamate was determined by measuring the absorbencies for mixtures of varying proportions of copper and the reagent. If only one product is formed, the proportion giving maximum absorption indicates the composition of the complex. If more than one product is formed, measurement at various wave lengths gives different results.

In the experiment the amounts of copper and reagent were varied from zero to one microgram-atom and diluted to 100 ml. with a pH 8, 18 °/oo Cl solution. The resulting absorbencies are shown in Figure 3. A maximum absorption at the ratio copper to diethyldithiocarbamate of 0.33 to 0.67 was observed at all wave lengths.

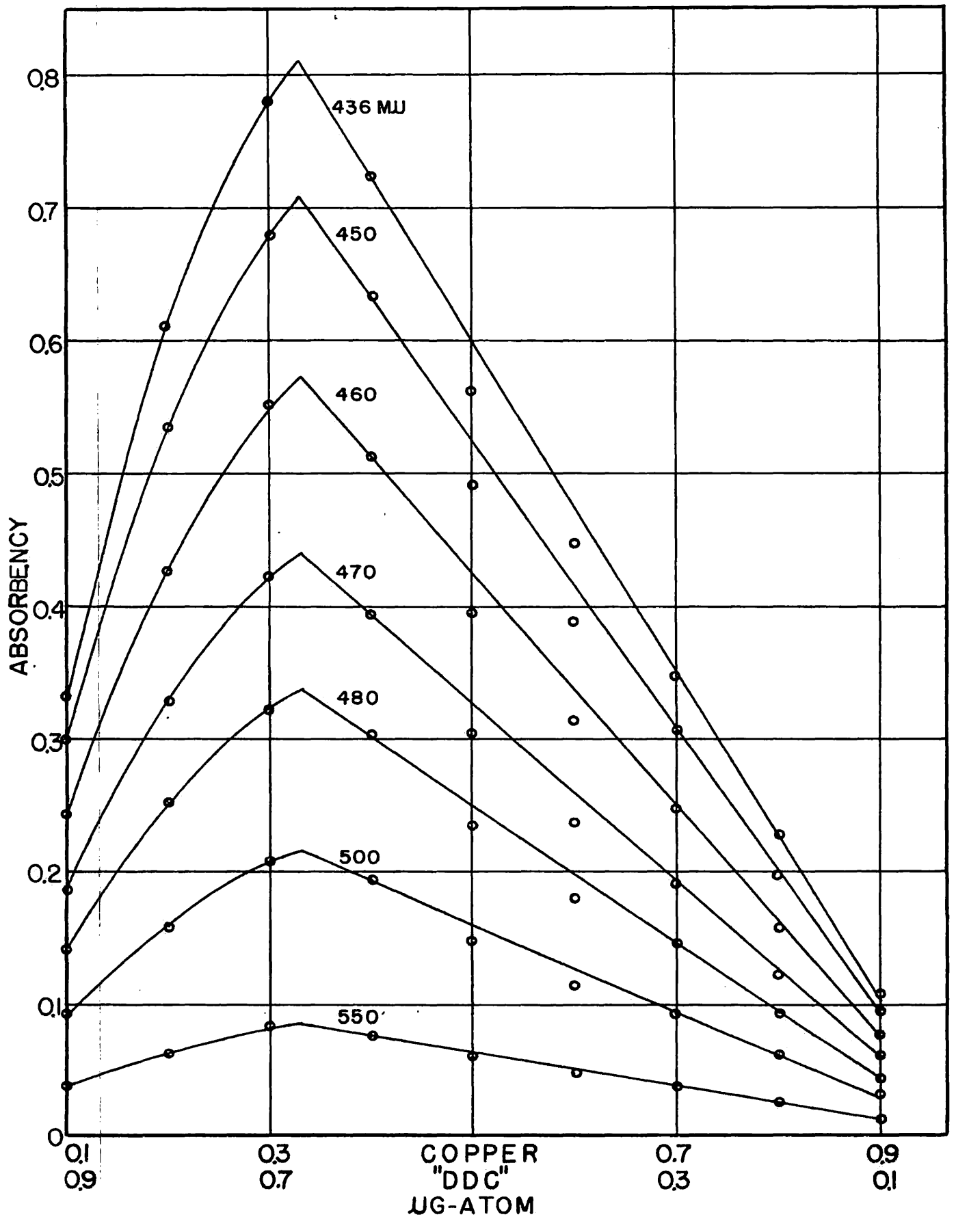
From the spectrophotometric study of copper diethyldithiocarbamate, it is concluded that the complex has a definite composition and only one compound is formed with a molar ratio of copper to diethyldithiocarbamate of one to two, regardless of whether it was formed from equivalent amounts of copper and diethyldithiocarbamate or with one in excess.

The chelate compound probably has the following structure



in which copper has replaced two sodium atoms. The two bidentate groups are presumed to occupy the four coordination positions of the metal through electron pairs furnished by the nitrogen atoms.

Figure 3: Composition of Copper Diethyldithiocarbamate Complex. Extracted from pH 8, 18 °/oo Cl solutions.


0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
ABSORBENCY
436 MU
450
460
470
480
500
550
0.1
0.9
0.3
0.7
COPPER
"DDC"
MG-ATOM
0.7
0.3
0.9
0.1

Effect of Amount of Reagent on Color Intensity

The effect of excess reagent on the color intensity is shown in Figure 4. Different amounts of sodium diethyldithiocarbamate solution and 0.25 microgram-atom of copper were added to 18 °/oo Cl, pH 8 solution and the copper complex was extracted with xylene for ten minutes. The observed absorbency increased sharply with increasing amount of reagent up to the equivalent point. The color intensity in xylene was not affected even by a thirty fold increase in excess of reagent.

Effect of Time on Extraction

The shaking time of extraction played an important role in the determination with considerable effect on the equilibrium of extraction as shown in Figure 5. Solutions, each containing 0.25 microgram-atom of copper, were shaken for varying time intervals and the absorbencies were determined. The absorption increased in the first ten minutes of shaking then leveled off and reached an equilibrium point after forty minutes.

Effect of Concentration on the Coefficient of Extraction

The completeness of extraction of copper at equilibrium was studied over a range of concentrations. The colored copper complex formed in pH 8, Cl 18 °/oo solution was extracted into xylene by the normal procedure. The aqueous solution was separated from xylene using a separatory funnel and was again extracted with another 5 ml. of xylene. The absorbencies of these two portions of xylene measured separately are shown in Table II. Calculation based on absorbency data showed the first extraction at equilibrium to be on average 97 per cent complete.

Figure 4: Effect of Amount of Reagent on Color Intensity. 0.25 microgram-atom of copper extracted from pH 8, 18 °/oo Cl solutions.

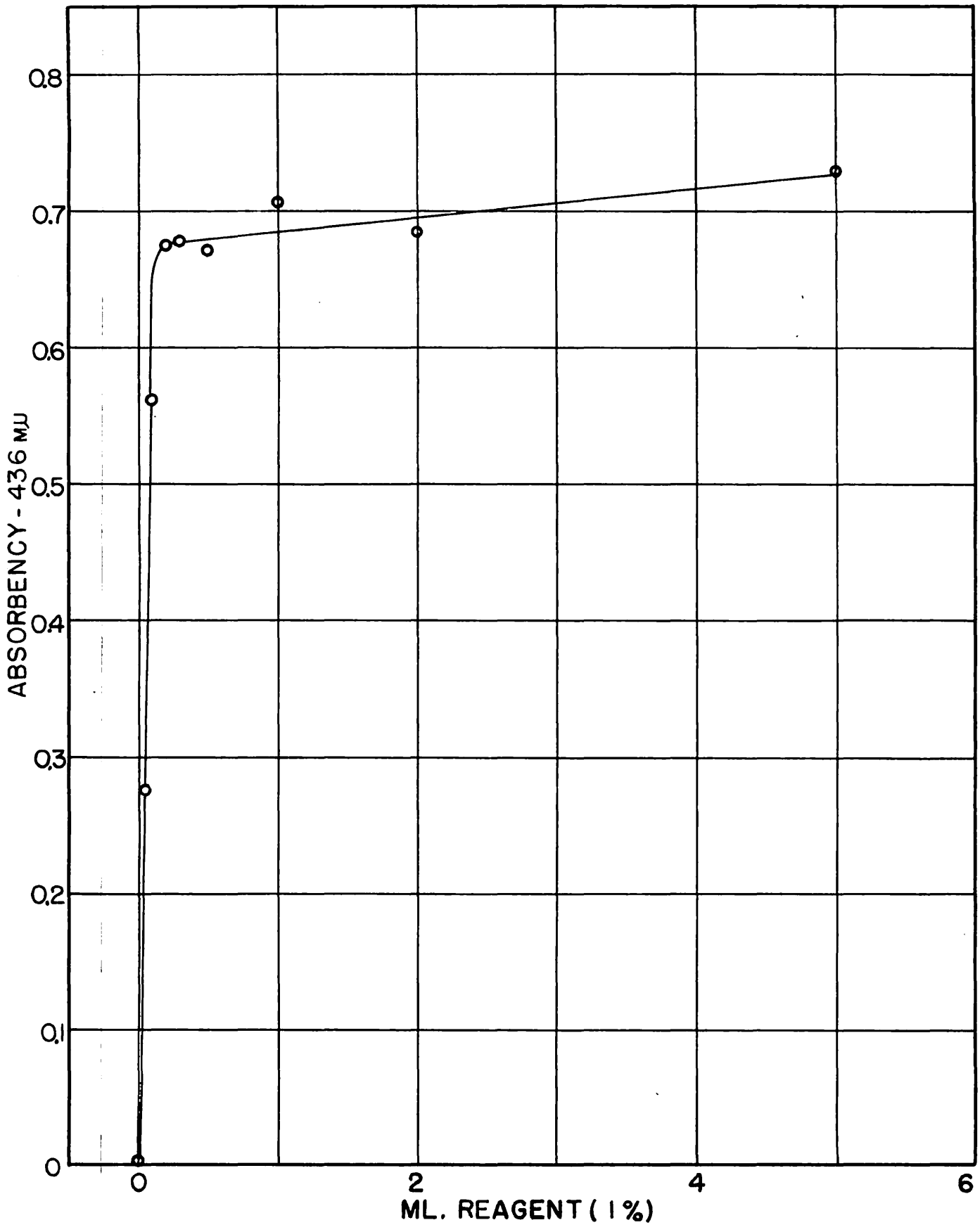

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
ABSORBENCY - 436 MU
0
2
4
6
ML. REAGENT (1 %)

Figure 5: Effect of Time on Extraction. 0.25 microgram-atom of copper extracted from pH 8, 18 °/oo Cl solutions.

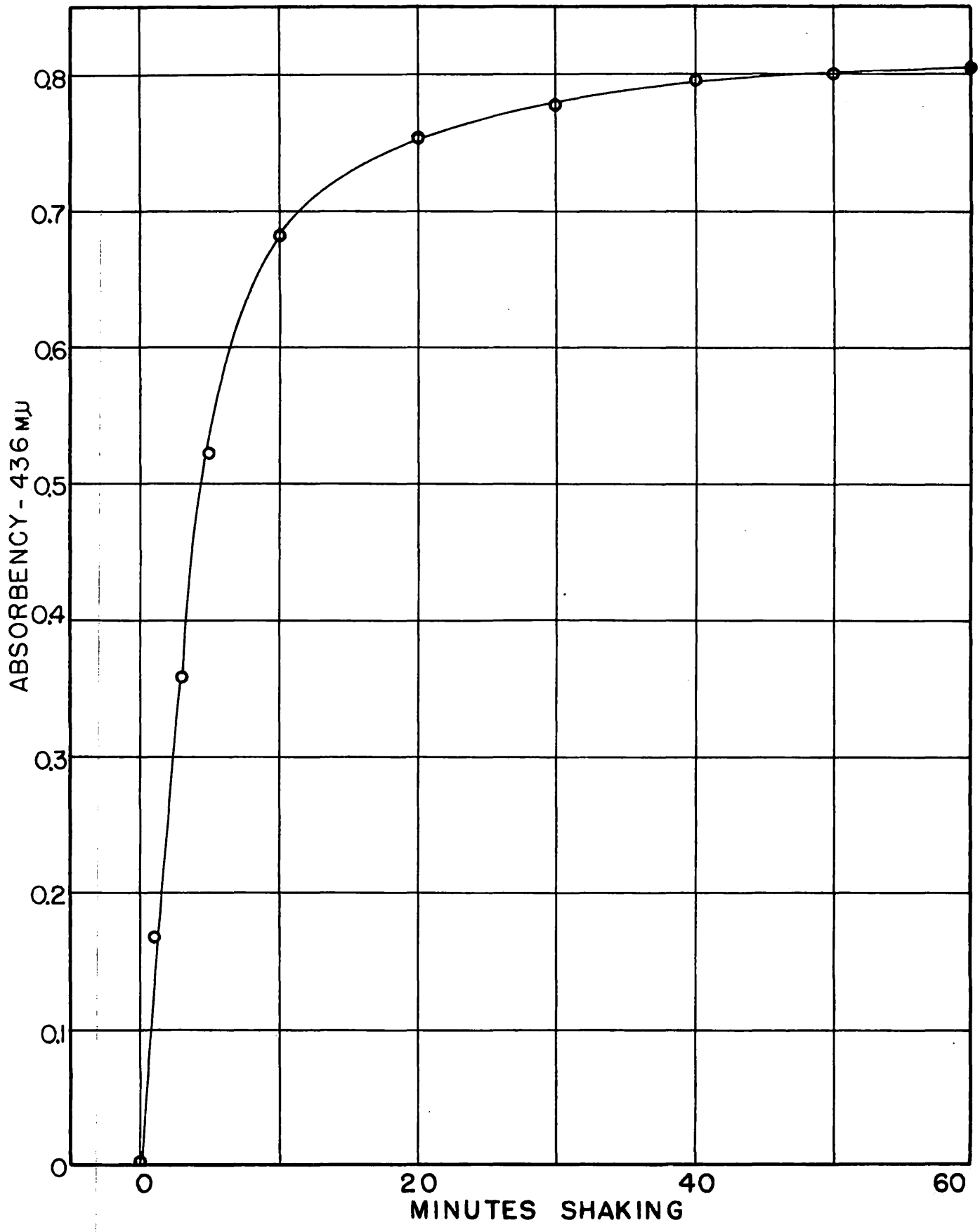

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
ABSORBENCY - 436 mμ
0
20
40
60
MINUTES SHAKING

TABLE II

Coefficient of Extraction

Copper Added Microgram-atom	Absorbencies 1st Extraction	2nd Extraction	Coefficient of Extraction
0.00	0.048	0.026	----
0.10	0.325	0.031	0.98
0.20	0.667	0.042	0.97
0.30	0.928	0.058	0.97
0.40	1.202	0.068	0.96
0.50	1.528	0.067	0.97

Effect of Hydrogen Ion Concentration on Color Intensity

Various amounts of copper ranging from 0.0 to 0.25 microgram-atom were diluted to 100 ml. with 18 °/oo Cl solution, and buffered to pH values of 7.0, 8.0, 9.0 and 10.0 respectively. The measured absorbencies of the copper complex in xylene showed the color intensity at given pH values to be a linear function of the copper concentration. The straight lines were parallel within two per cent per unit of pH, less than the experimental error. The solution with the lowest pH value showed the largest blank. The slight change of pH in sea water as it occurs naturally would not affect the determination.

Effect of Salinity* on Color Intensity

This effect was determined by buffering solutions containing varying amounts of copper to pH 8, adjusting their chlorinities from 0 to 18 °/oo and measuring the absorbencies.

* Salinity = 0.030 + 1.805 Cl °/oo.

A linear relationship was found between absorbency and copper concentration with slopes deviating about one per cent for a change of 10 °/oo Cl. The seasonal fluctuations of salinity of sea water are in general less than this and therefore would not affect the accuracy of the determination.

Effect of Oxidizing and Reducing Agents on Color Intensity

Reactions were carried out by the normal procedure in the pH 8, Cl 18 °/oo solutions with various amounts of copper. Four ml. of 3% hydrogen peroxide in one case and four ml. of 3% hydroxylamine in another were introduced respectively as oxidizing and reducing agents. Absorbencies plotted against copper concentration were linear with a deviation in slope of approximately two per cent for both the oxidizing and reducing agents.

Effect of Interfering Elements

Individual solutions of various metallic ions, each with a concentration of 0.25 microgram-atom per milliliter, were prepared in order to test the reaction of the diethyldithiocarbamate at various pH values from 5 to 10. The reactions obtained are summarized:

pH	Cu^{+2}	Ni^{+2}	Co^{+2}	Bi^{+3}	Mn^{+2}	UO_2^{+2}	$Fe^{+2,+3}$
5	Brown ppt.	Pale green ppt.	Green ppt.	Pale green ppt.	Pink ppt.	Yellow color	Purple ppt.
7	"	"	"	"	"	"	"
8	"	"	"	"	"	"	No ppt.
9	"	"	"	"	"	No color	No ppt.
10	"	"	"	"	No ppt.	"	No ppt.

Ferric and ferrous ions gave purple precipitates with sodium diethyldithiocarbamate in acid solution but not in the pH range of sea water. Uranyl diethyldithiocarbamate showed a yellowish color which did not dissolve in xylene. Manganese formed a pink precipitate with the reagent and it was extractible in xylene to give a purple solution. A small quantity of manganese did not interfere in the determination because the purple color was very unstable in xylene and faded quickly. Up to 0.25 microgram-atom of iron, uranium and manganese did not cause any appreciable increase in absorbency.

In alkaline solution, but not in acid, cyanide ions formed an extremely stable copper cyanide complex preventing the reaction of copper with diethyldithiocarbamate. The cyanide ion does not occur in sea water.

Bismuth, cobalt and nickel occur in sea water in insufficient concentrations to interfere with the determination of copper, but may possibly interfere with the analyses of marine organisms and bottom sediments. The optical absorption spectra of the respective complexes of these elements in xylene extracted from solutions of Cl 18 °/oo and different pH value are shown in Figure 6, 7, and 8. The nickel complex shows maxima at wave lengths of 325 mμ and 390 mμ and was not affected by changing the hydrogen ion concentration. The complexes show maximum absorption at 325 mμ for cobalt and 305 and 365 mμ for bismuth. The wave lengths of maximum absorption of these complexes did not change with pH but their magnitudes were depressed considerably with increasing pH values.

A series of standard calibration graphs of bismuth, cobalt and nickel complexes at the wave length of 436 mμ and also at their maximum

Figure 6: Absorption Spectrum of Nickel Diethyldithiocarbamate in Xylene. 0.25 microgram-atom of nickel extracted from Cl 18 °/oo solution at various pH values.

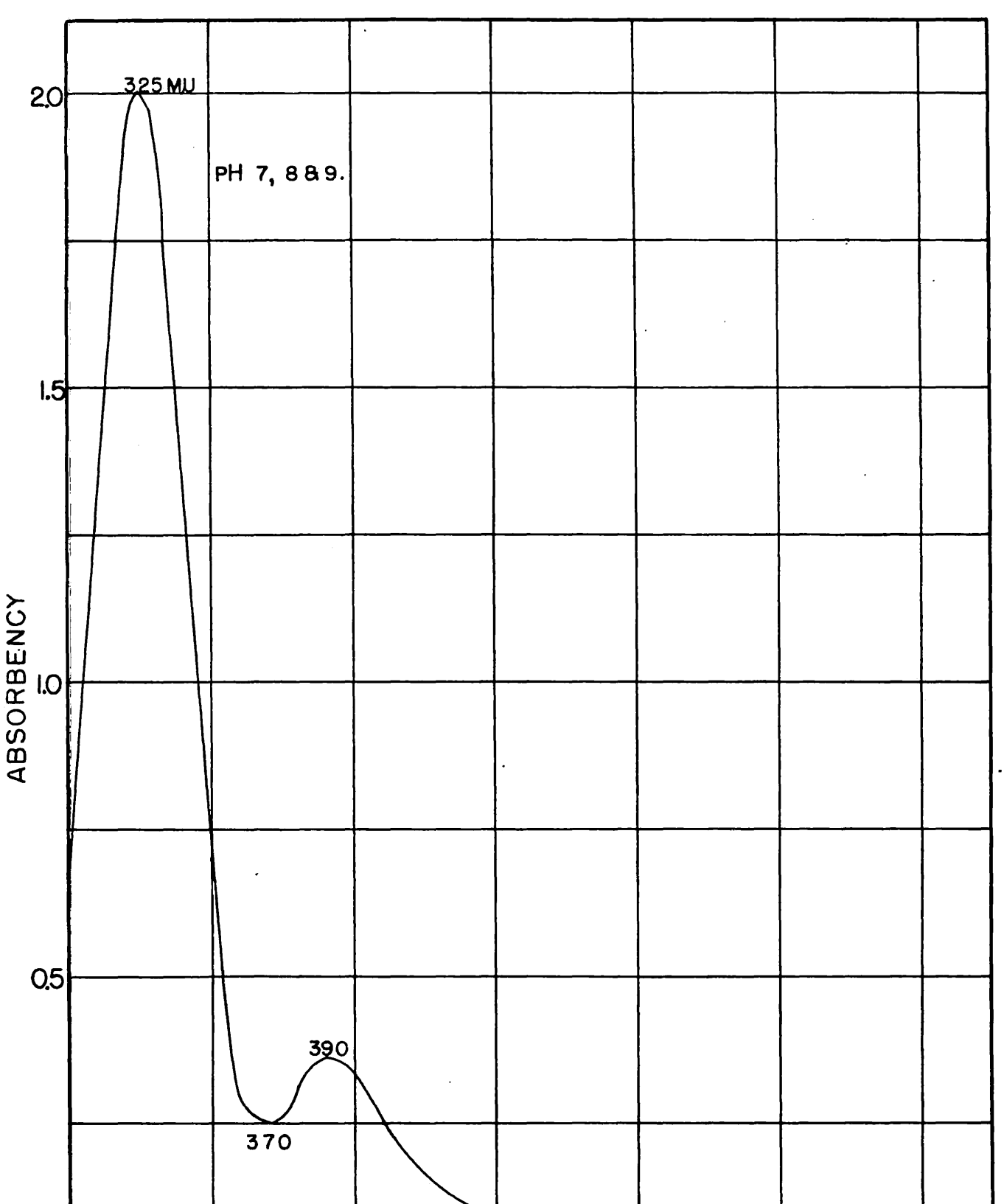

325 MU
PH 7, 8 & 9.
2.0
1.5
1.0
0.5
0
ABSORBENCY
390
370
300
400
500
600
WAVELENGTH, MU

Figure 7: Absorption Spectrum of Cobalt Diethyldithiocarbamate in Xylene. 0.25 microgram-atom of cobalt extracted from Cl 18 °/oo solution at various pH values.

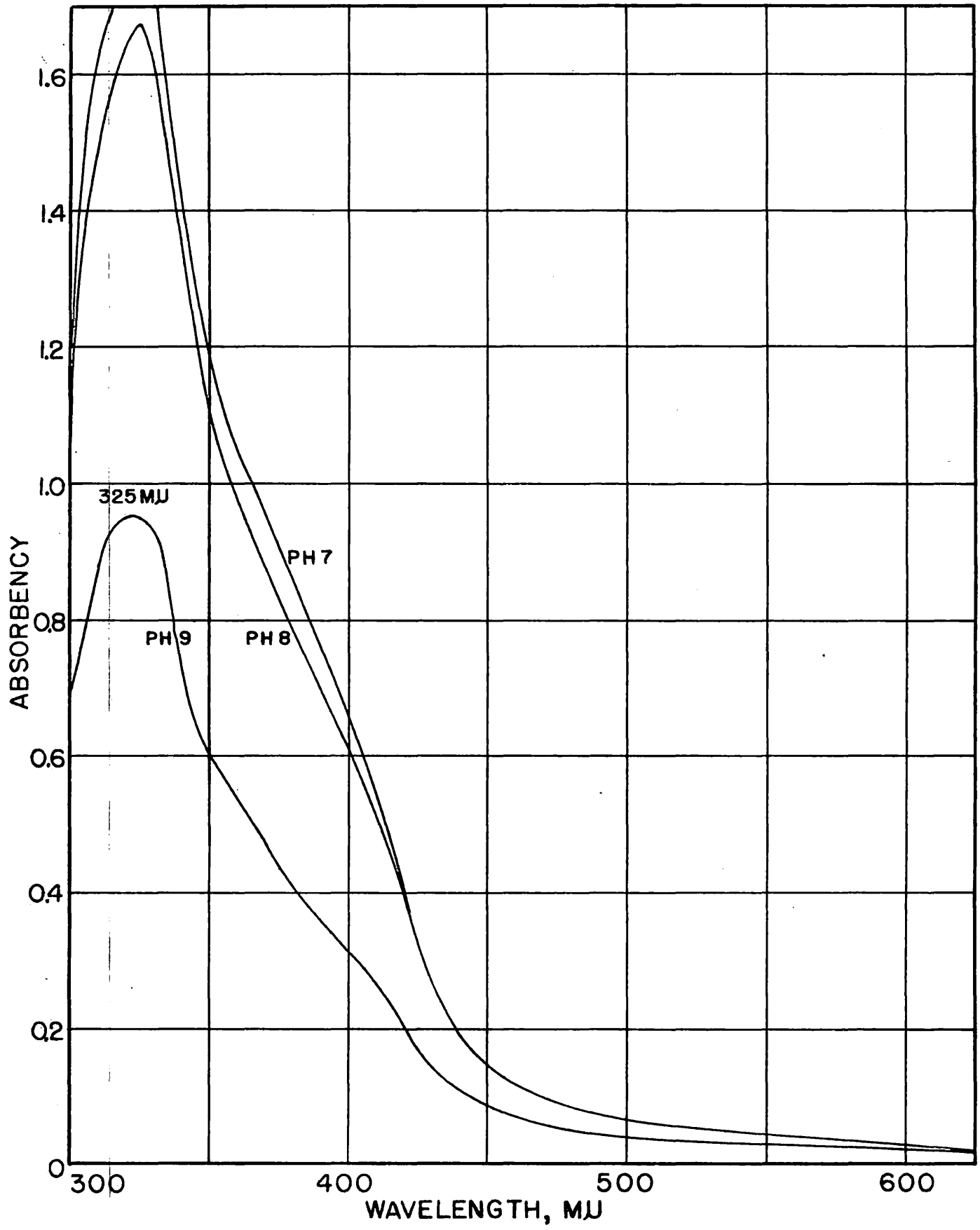
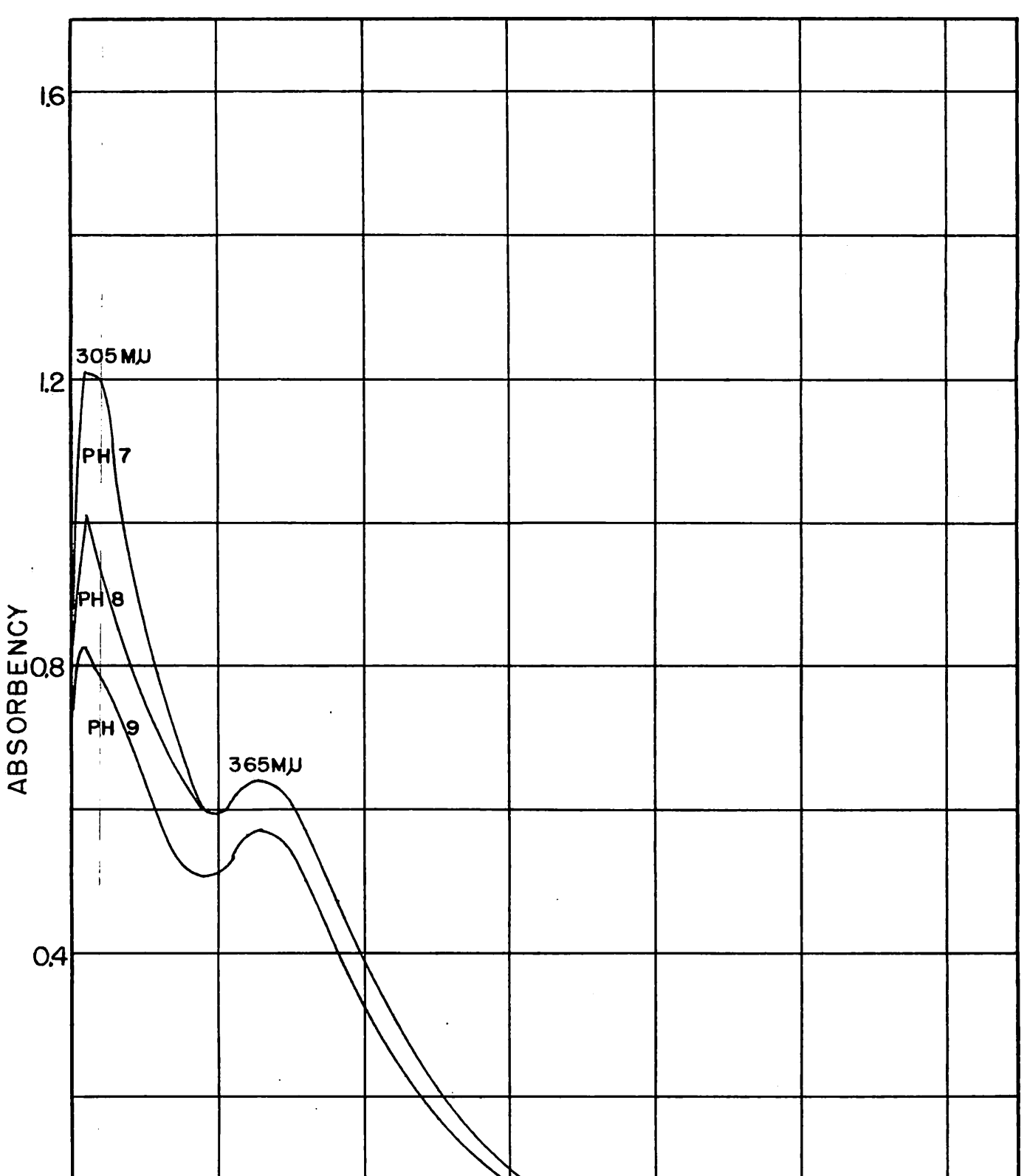

1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
ABSORBENCY
325 MU
PH 7
PH 9
PH 8
300
400
500
600
WAVELENGTH, MU

Figure 8: Absorption Spectrum of Bismuth Diethyl-dithiocarbamate in Xylene. 0.25 microgram-atom of bismuth extracted from Cl 18 °/oo solution at various pH values.


1.6
1.2
0.8
0.4
0
ABSORBENCY
305 MU
PH 7
PH 8
PH 9
365MU
300
400
500
600
WAVELENGTH, MU

absorption peaks were prepared. Varying quantities of each of these elements ranging from 0.0 to 0.25 microgram-atom were treated with sodium diethyldithiocarbamate reagent by the described procedure. The resulting absorbencies plotted against the concentrations of the respective elements are shown in Figure 9. The linear graphs obtained enable the application of correction for these interfering substances in the copper determination. The concentrations of bismuth, cobalt and nickel can be ascertained by noting the absorbencies at the respective maximum absorption wave lengths. The appropriate corrections to be applied to the absorbency at the wave length of 436 mμ are as follows:

Wave length mμ	Element 1 microgram-atom	Corresponding to Cu Microgram-atom at 436 mμ
436	Bi	0.16
436	Co	0.21
436	Ni	0.14
365	Bi	0.77
325	Co	1.85
325	Ni	2.32

Cobalt and nickel seriously interfere with the determination of copper if present in appreciable amounts. Dimethylglyoxime was added in an attempt to minimize these interferences. Diethyldithiocarbamate reagent was added to solutions containing varying quantities of nickel ranging from 0.0 to 0.25 microgram-atom in the presence of dimethylglyoxime. Absorbencies of these xylene extracts were measured by the normal procedure.

Figure 9: Calibration Graphs for Bismuth, Cobalt and Nickel Diethyldithiocarbamates. Extracted from pH 8, 18 °/oo Cl solutions.

Slopes: At 436 mμ, BiDDC 0.52

CoDDC 0.70

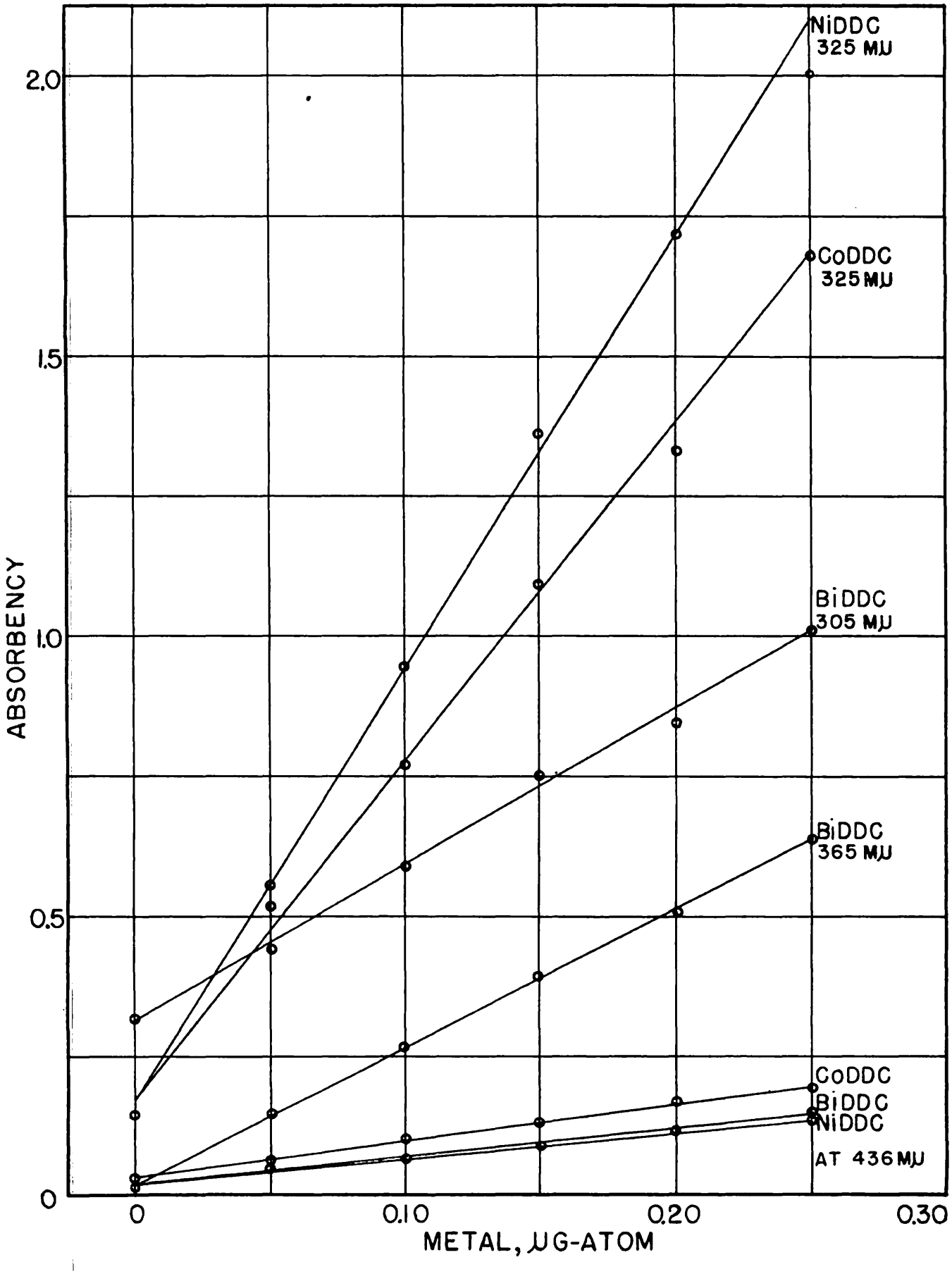
NiDDC 0.47

At 325 mμ, CoDDC 6.77

NiDDC 7.74

At 365 mμ, BiDDC 2.44

At 305 mμ, BiDDC 2.78 units absorbency per microgram-atom.


NiDDC
325 MU
CoDDC
325 MU
BiDDC
305 MU
BiDDC
365 MU
CoDDC
BiDDC
NiDDC
AT 436 MU
2.0
1.5
1.0
0.5
0
ABSORBENCY
0
0.10
0.20
0.30
METAL, UG-ATOM

Nickel dimethylglyoxime is sparingly soluble in xylene showing a faint pink color. The absorbency reading of the saturated solution at the wave length of 436 mμ corresponded to 0.05 microgram-atom of copper.

The solubility of the yellowish cobalt dimethylglyoxime is far less than that of nickel. The increase in absorbency at the wave length of 436 mμ due to the presence of 10 microgram-atoms of cobalt corresponded to 0.03 microgram-atom of copper.

The validity of the method of correcting for interfering elements was tested on known solutions containing 0.25 microgram-atom of copper and equal amounts of bismuth, cobalt and nickel in 100 ml. solutions with pH 8, 18 °/oo Cl. The absorbencies of the xylene extract measured by the normal procedure are summarized as follows:

Elements Added Microgram-atom				Absorbencies at 436 mμ		
Cu	Bi	Co	Ni	Observed	Corrected for Blank	Corrected for Interfering Ions
.00	.00	.00	.00	.050	.000	.000
.25	.00	.00	.00	.835	.785	.785
.25	.25	.00	.00	.967	.917	.790
.25	.00	.25	.00	1.014	.964	.795
.25	.00	.00	.25	.945	.895	.786
.25	.25	.25	.25	1.255	1.205	.797

Calibration Graphs for Sea Water

A sea water surface sample showing a pH value of 7.8 and a salinity of 30.9 °/oo was taken during high tide at Friday Harbor, Washington on July 19, 1951. A standard calibration graph was prepared by adding various

quantities of copper ranging from 0.0 to 0.20 microgram-atom to 500 ml. of sea water. The absorbency readings measured as previously described using an absorption cell of 1 cm. optical path are plotted against copper concentrations in Figure 10. The slope * of the line was found to be 3.35 units absorbency reading per one microgram-atom of copper. A corrected absorbency reading of 0.005 was calculated to correspond to 0.0015 microgram-atom of copper in a 500 ml. sea water sample. The blank varied with the particular sea water used and corresponding correction should be made when reading the copper content directly from the calibration graph.

In studying the possible presence of elements which would interfere in the determination of copper in sea water, a sample was extracted by the normal procedure and the absorption spectrum measured at different wave lengths over the range from 300 mμ to 700 mμ. These results, shown in Figure 11, exhibit maximum absorptions at 436 mμ and approximately 300 mμ due respectively to copper and excess of the reagent. The spectrum showed no evidence of bismuth, cobalt or nickel.

An examination has been made of more than 100 samples of surface sea water collected periodically near Friday Harbor and Seattle, Washington. The average concentration of copper in these waters, expressed in microgram-atom per liter, was found to be 0.020 with a range from 0.012 to 0.030. Several fresh water lakes examined showed about 0.070 microgram-atom per liter

---

* The molar extinction coefficient of the copper complex in xylene is calculated to be 16,800/cm./mole.

Figure 10: Copper Calibration Graph for Sea Water.

July 19, 1951 High Tide, pH 7.8, Salinity 30.9 °/oo.

Slope = 3.35 units absorbency per microgram-atom of copper.

0.005 absorbency = 0.0015 microgram-atom of copper in 500 ml. sea water sample.

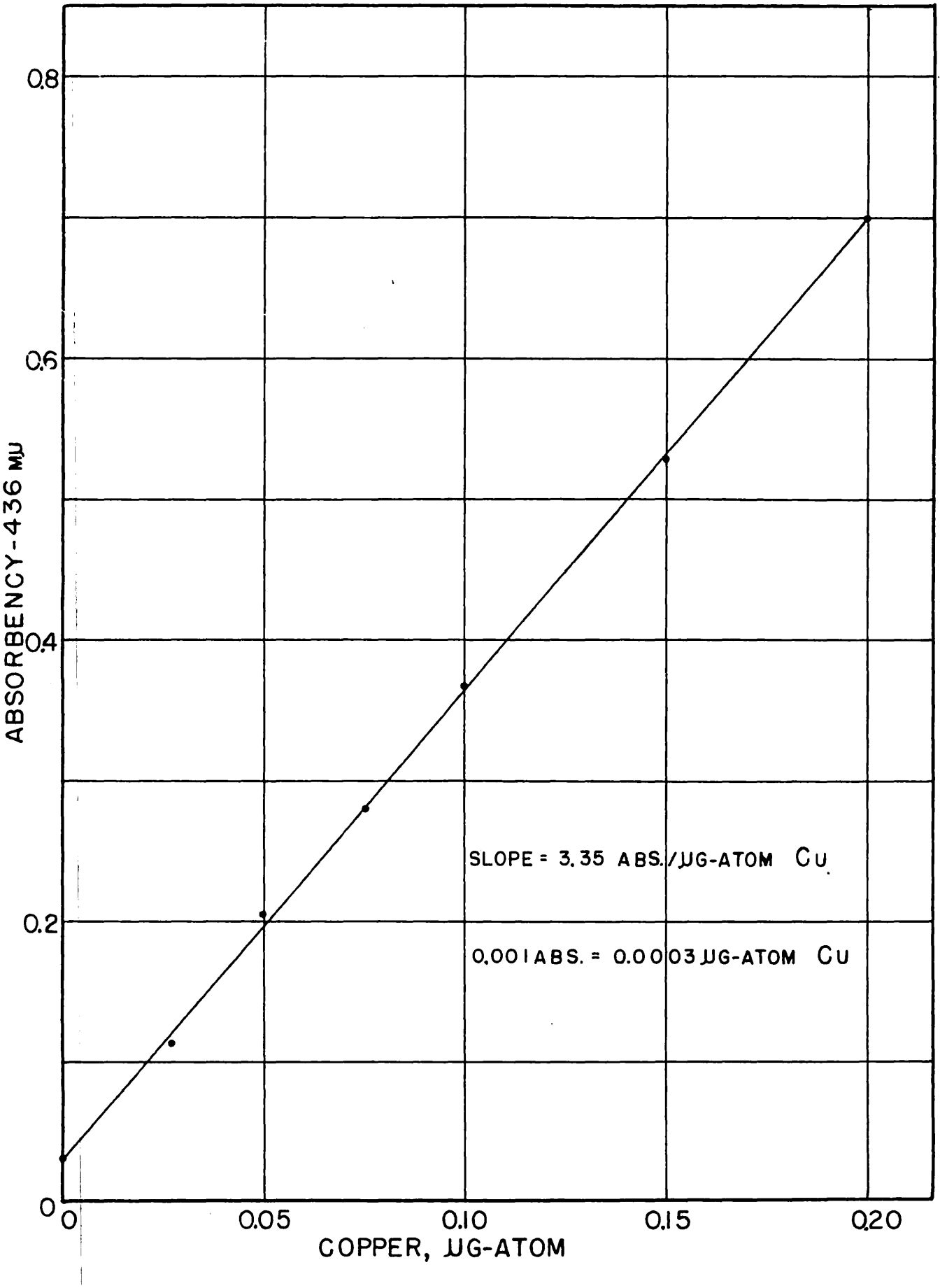
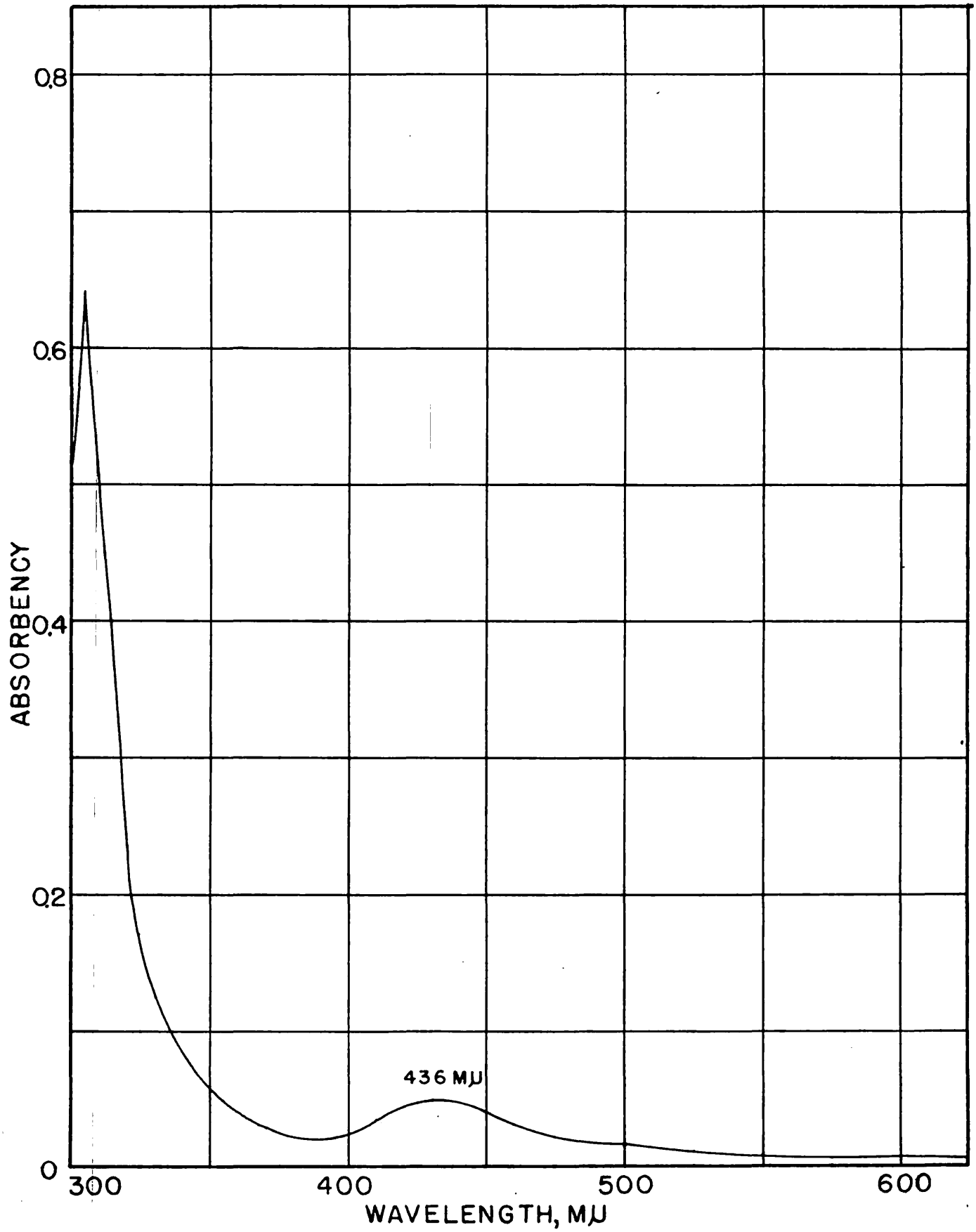

0.8
0.6
0.4
0.2
0
ABSORBENCY-436 MU
0
0.05
0.10
0.15
0.20
COPPER, UG-ATOM
SLOPE = 3.35 ABS./UG-ATOM Cu
0.001 ABS. = 0.0003 UG-ATOM Cu

Figure 11: General Absorption Spectrum for Sea Water Extracted with Diethyldithiocarbamate and Xylene.
July 19, 1951 High Tide, pH 7.8, Salinity 30.9 °/oo


0.8
0.6
0.4
0.2
0
ABSORBENCY
436 MU
300
400
500
600
WAVELENGTH, MU

The authors are now investigating the copper content in lakes and rivers of Washington State, sea sediments, and marine organisms, and its seasonal fluctuation at different depths in the sea, in coastal and offshore localities. The findings obtained will be given in Part II of this report.

SUMMARY AND CONCLUSIONS

1. Sodium diethyldithiocarbamate has been studied spectrophotometrically as a reagent to determine copper in sea water and found to be preferable to diphenylthiocarbazone (dithizone).

2. Increased sensitivity has been attained by extracting the colored copper complex with xylene. The useful lower limit of this method is approximately 0.002 microgram-atom of copper.

3. The effects of amount of reagent, hydrogen ion concentration, salinity, oxidizing and reducing agents on the color system have been examined and shown to have no influence on the accuracy of the determination. The coefficient of extraction has also been studied.

4. The diethyldithiocarbamate reagent has been found stable in ammoniacal solution. The colored copper complex in xylene shows no change after standing in diffused light for 48 hours, and is far more stable than the color produced with dithizone.

5. The composition of the copper complex has been determined by the continuous variation method. It is a definite compound with a molar ratio of copper to diethyldithiocarbamate of one to two.

6. The general absorption spectrum of sea water extract with the reagent in xylene has been examined showing an absence of interfering metals.

7. Bismuth, cobalt, iron, manganese, nickel, uranium and cyanide have been shown to interfere in the copper determination but not at the concentration of these substances found in sea water. A procedure has been devised for minimizing the interference, should the method be applied to the

analyses of marine organisms, bottom sediments or other materials.

8. A calibration graph for sea water has been prepared. A corrected absorbency reading of 0.005 has been found to correspond to 0.0030 microgram-atom of copper per liter in sea water. The molar extinction coefficient of the copper complex in xylene at the wave length of 436 mμ has been calculated to be 16,800/cm./mole.

ACKNOWLEDGEMENT

The authors wish to express their appreciation to Dr. Emery F. Swan for collecting sea water samples at Friday Harbor, Washington and to Dr. Rex J. Robinson for his valuable suggestions. They are also indebted to Drs. Clifford A. Barnes and Maurice Rattray, Jr. for reading the manuscript.

LITERATURE CITED

Atkins, W. R. G.
1932. The copper content of sea. J. Marine Biol. Assoc., 18:193-7.

1933. The rapid estimation of the copper content of sea water. J. Marine Biol. Assoc., 19: 63-6.

Bardet, Jacques, Arakel Tchakirian and Raymonde Lagrange
1938. Spectrographic search for traces of elements in sea water. Comp. rend., 206: 450-2.

Barnes, H. and Lord Rothschild
1950. A note on the copper content of sea urchin semen and sea water. J. Expt. Biol., 27 (2): 123-5.

Black, W. A. P. and R. L. Mitchell
1952. Trace elements in the common brown algae and in sea water. J. Marine Biol. Assoc., 30: 575-84.

Brown, W. E.
1942. The analysis of copper in sea water. Thesis, University of Washington, Seattle.

Buch, Kurt
1944. Dithizone method for determining copper and zinc in natural water. Finska Kemistsamfundets Medd., 53 (1-2): 25-37.

Dieulafait, M. L.
1879. Le cuivre. 2ieme parte, chapitre 1. Cuivre dans les eaux des mers de tous les ages, et concentration de ce metal dans certains de leurs depot. Ann. Chim. Phys., 18 (5 serie): 359-64.

Delepine, Marcel
1908. Sulfur and nitrogen compounds from carbon disulfide. XII. Metallic thiosulphcarbamates. Bull. soc. chim., 3: 643-52.

Galtsoff, P. S.
1943. Copper content of the sea. Ecology, 24: 263-5.

Hiltner, R. S. and H. J. Wichmann
1919. Zinc in oysters. J. Biol. Chem., 38: 205-21.

Isibasi, Masayosi, Kozo Kurata and Tugio Hirobe
1940. Chemical studies of the ocean. VII. Quantitative determination of copper in sea water and bittern. J. Chem. Soc. Japan, 61: 726-8.

Kalle, Kurt and Hermann Wattenberg
1938. The copper content of ocean water. Naturwissenschaften, 26: 630-1.

Koroleff, Folke
1950. Determination of traces of heavy metals in sea water by means of dithizone. Merentutkimuslaitoksen Julkaisu Havsforskning Institutets Skrift (145).

Meulen, H. ter
1931. Distribution of molybdenum in nature. Rec. trav. chim., 50: 491-504.

Meyer, Helga
1938. Die photometrische Bestimmung des Kupfers in Seewasser. Annalen der Hydrographie and Martimen Meteorogie, 49: 325-30.

Morita, Yoshimi
1950. Distribution of copper and zinc. IV. Copper and zinc contents of sea water. J. Chem. Soc. Japan, Pure Chem. Sect., 71: 246-8.

Murakami, Yukio
1950. Modified colorimetric determination of copper with sodium diethyldithiocarbamate in the presence of hydroxylamine. Bull. Chem. Soc. Japan, 23 (1): 3-7.

Noddack, Ida and Walter Noddack
1939. Die Haufigkeiten der Schwermetalle in Meerestieren. Arkiv for Zoologi, Band 32A (4): 1-35.

Orton, J. F.
1923. An account of investigation into the cause of the umusual mortality among oysters in English oyster beds during 1920-1. Ministry of Agri. and Fish. Invest. London, 6 (3-4).

Prytherch, H. T.
1934. The role of copper in the setting, metamorphosis and distribution of the American oysters. Ecological Monographs, 4: 47-107.

Riley, G. A.
1937-1938. The significance of the Mississippi River drainage for biological conditions in the northern Gulf of Mexico. J. Marine Research, 1 (1): 60-74.

Rose, W. C. and Meyer Bodansky
1920. Biochemical studies on marine organisms. I. The occurrence of copper. J. Biol. Chem., 44: 99-112.

Severy, H. W.
1923. The occurrence of copper and zinc in certain marine animals. J. Biol. Chem., 55: 79-92.

Woodbridge, C. G.
1938. The distribution of copper in sea water. Thesis, University of Washington, Seattle.

Technical Report No. 9 Distribution List - University of Washington

1 - Dean Harold W. Stoke
Graduate School
3 Administration Bldg.

1 - Dean Lloyd S. Woodburne
College Arts & Science
122 Thomson Hall

4 - Mr. Lawrence P. Murphy
Fisheries-Oceanography Library
Fisheries Center

1 - Dr. Richard H. Fleming
Oceanography
202 Ocean. Labs.

1 - Dr. Thomas G. Thompson
Oceanography
318 Ocean. Labs.

1 - Dr. Clifford A. Barnes
Oceanography
201 Ocean. Labs.

1 - Dr. Emery F. Swan
Oceanography
Friday Harbor, Washington

1 - Dr. Maurice Rattray, Jr.
Oceanography
308 Ocean. Labs.

1 - Dr. Robert G. Paquette
Oceanography
209 Ocean. Labs.

1 - Dr. Rex J. Robinson
Chemsitry
113 Bagley Hall

1 - Arthur W. Martin
Zoology
140 Johnson Hall

1 - Dr. Erling J. Ordal
Microbiology
B 307 Health Science Bldg.

1 - Michael Waldichuk
Oceanography
316 Ocean. Labs.

1 - Miss Doris Stewart
Zoology
Johnson Hall

1 - Kerry Yasunobu
Biochemistry Lab.
Health Science Bldg.

1 - Tsaihwa J. Chow
Chemistry
216 Ocean. Labs.