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Title: EXTRACTION OF ZINC FROM SEA WATER

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A liquid-extraction procedure for the concentration of zinc in sea water was developed. The metal ion in sea water was chelated with sodium diethyldithiocarbamate and extracted into an organic solvent, methylisobutylketone, at the normal pH of sea water. A back-extraction into HCl followed, providing a concentration of 30X for the entire procedure.

Filtration was introduced into the procedure to insure that only dissolved forms were extracted and that no influence from particulate matter would be detected. Problems of loss of zinc and/or contamination arose. These were overcome to a great extent by washing all glassware, including the sintered-glass filter holder, in nitric acid and by following the filtration through the glass holder with an acid rinse. Purification of reagents was found necessary.

With replicate analyses on a given sea water source, the recovery was $97 \pm 2\%$. Upon making varying standard additions to subsamples of sea water, the calculated recovery was $97 \pm 5.4\%$. The contamination figure for the extraction process ranged from zero to 0.8 ppb in the original sea water sample. With filtration, an overall median contamination of 1.4 ± 1 ppb was determined.

Extraction of Zinc From Sea Water

by

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EXTRACTION OF ZINC FROM SEA WATER

INTRODUCTION

General Statement

A simple but dependable ship-board method of analysis for stable zinc in sea water is required for specific-activity measurements of radioactivity. Zinc, however, is present in sea water in trace concentrations varying from about 0.5 to 50 $\mu\text{g/l}$ (10^{-8} to 10^{-6} M) (Goldberg, 1965). These values are too low for most methods of analysis without prior concentration. A relatively rapid and straightforward method of concentrating trace metals, and one which has proven applicable to zinc in sea water, is liquid-liquid extraction. This type of extraction as used here refers to a two-layered system of immiscible aqueous and organic solvents. The zinc in the aqueous medium (sea water) is extracted into a smaller volume of organic solvent. Thus, both separation and concentration of the zinc are accomplished.

Background Information

Solvent Extraction

The principles of solvent extraction are based on several generalities. First, in the dipolar water medium, zinc ions and other

ionic species tend to be soluble due to the polar water molecules aiding in the separation of oppositely-charged ions. In organic solvents, however, an uncharged species has the advantage. Here, the dissolving process is often more physical than chemical, and the rule of "like dissolves like" is usually applicable. In the specific case of Zn^{++} , introduction of a water-soluble chelate, sodium diethyldithiocarbamate, results in the formation of an uncharged zinc-chelate species which is quantitatively extractable into the organic solvent.

Chelation

The chelate used, sodium diethyldithiocarbamate (DEDTC), contains both an anionic site and an uncharged basic site, thus satisfying the charge requirements of zinc: $(\text{C}_2\text{H}_5)_2\text{-N-C}\begin{smallmatrix} \text{S} \\ \diagup \\ \text{S} \end{smallmatrix}\text{Zn}\begin{smallmatrix} \text{S} \\ \diagdown \\ \text{S} \end{smallmatrix}\text{C-N-}(\text{C}_2\text{H}_5)_2$ (Terent'ev, et al.). The pK_{sp} of this complex is 30 (Kemula and Hulanicki, 1961), and even with the trace quantities of zinc present in sea water, the zinc carbamate will precipitate in the aqueous phase. The complex is soluble in the organic solvent methylisobutyl ketone (MIBK), however, and is quantitatively extracted from the sea water into the MIBK.

A further concentration in this case may be attained by back-extraction from the organic phase into an aqueous acid phase. The

acid functions to decompose the chelate, bringing the zinc ions into the aqueous polar phase.

Atomic Absorption

The final analysis of the concentrated zinc in the acid phase is accomplished on the Perkin-Elmer Model 303 Atomic Absorption Spectrometer (AAS). This instrument is similar to an infra-red spectrophotometer with the infra-red source replaced by a hollow-cathode discharge lamp of the element (in this case Zn) plus modification of the optics. Also, a direct aspirator-type burner for the production of oxyacetylene flames is necessary. Light from the lamp includes spectral lines of the element. These are focused into the flame, then into a monochromator to separate out one line, and finally into a photomultiplier tube for detection and readout. Only the atoms of the given element will absorb light from the lamp when aspirated into the burner and flame. This light is chopped and compared with light not passed through the flame, and a percent absorption (a) figure is recorded. A standard curve of absorbance ($A = 100 \log 1/(1-a)$) versus parts per million (ppm) must be run with each group of experimental samples due to continual change in the curve resulting from subtle changes in the settings on the AAS between runs. The curve follows Beer's law, but the percent absorption readings from the instrument do not form a perfectly straight

line when absorbances are plotted against ppm. Instead, a slight curvature is noted in the outlined absorbance points. Samples of standard curves of absorbance versus ppm are given in Figure 6. The standard curve line from zero to one ppm actually approximates a slight curve.

Species Extracted

The question of exactly what form or species of zinc is being extracted presents a problem. Ideally, if the rate constants allow, all inorganic forms of zinc present in the sea water would be extracted. This is due to the fact that the drive towards equilibrium during the extraction of Zn^{++} should force the reactions toward the ionic species, Zn^{++} . If organic matter is present, the procedure might also draw zinc from this source, though it is very unlikely that this occurs to the same extent as in the inorganic species. In fact, it is very doubtful that all inorganic forms are extracted, as the rate constants do not all allow for full extraction to be achieved in the time given for equilibrium (about one hour).

Analyses for Zinc in Sea Water

There are a variety of methods for the analysis of trace quantities of zinc. An old favorite is the dithizone (diphenyldithiocarbazone) colorimetric technique practiced by Vallee and Gibson

(1950). At the proper pH, zinc plus dithizone yields a bright red keto complex soluble in CCl_4 or CHCl_3 . The complex has an absorption peak at 520 $\text{m}\mu$, while the green dithizone in CCl_4 has its maximum absorbance at 620 $\text{m}\mu$. The ratio of relative absorbances at 620 and 520 $\text{m}\mu$ can be determined, and by comparing with a calibration standard, sample concentration of an unknown may be found.

Other workers (e. g. Black and Mitchell, 1951) used emission spectrography for trace analysis of zinc. A third method, the direct use of an AAS (Fabricand, 1962) required a modified AAS of extreme sensitivity. A method becoming more prominent is activation analysis (Rona and Hood, 1962). Hood performed total zinc precipitation by co-precipitation with $\text{Fe}(\text{OH})_3$ and followed this with bombardment with slow neutrons. Hood also analyzed for ionic zinc by liquid extraction into chloroform with sodium diethyldithiocarbamate as the chelating agent. These samples, also, were activated in a flux of slow neutrons. After further purification, the samples were counted with a 3x3-inch $\text{NaI}(\text{Tl})$ solid scintillation crystal in a 256-channel analyzer. Again, use of calibration standards was necessary.

A method recently applied to the analysis of zinc in sea water is liquid/liquid, discontinuous, countercurrent solvent extraction. R. R. Brooks (1965b) filtered his samples and oxidized them with chlorine water. This formed the moving upper phase in the countercurrent extraction. The lower stationary phase was a 1% solution of

8-quinolinol in chloroform. The apparatus was run through 400 transfers of increasing extraction. When the organic phases were summed and taken to dryness, the samples were analyzed spectrochemically in the d. c. arc. His results gave a concentration factor of 400,000 with a variation of 10%. The equipment was elaborate, however, and the procedure would be most unsatisfactory for ship-board use (Brooks, 1965a).

The procedure similar to that originally used in this project was described by Joyner and Finley (1966) for the determination of manganese and iron in sea water. Their procedure began with the addition of 10 ml of 5% sodium DEDTC to 200 ml of sea water containing known amounts of Mn and Fe. Fifteen minutes later they added 10 ml of MIBK and mixed for two minutes. This was then allowed to separate for 20 minutes. The final separation of the two layers was accomplished with the aid of a centrifuge. Direct analysis on the AAS followed.

Correlation of Zinc Values

Previous attempts at correlation of data on zinc have met with little success. The data are usually given in μg of Zn^{++} per liter versus depth, season, salinity, time, weather, and/or geographic location. Chipman, Rice and Price (1958) and Fonselius and Koroleff (1963) were among a minority of workers who noted a

consistent variation in their data. Chipman's values, all of surface samples from the coastal waters off Beaufort, North Carolina, indicated a seasonal correlation (Table 1). No explanation for this variation was known. After one hurricane, the zinc value increased considerably, however, and was explained as resulting from fresh-water pollutant. This is typical near coasts with any degree of runoff.

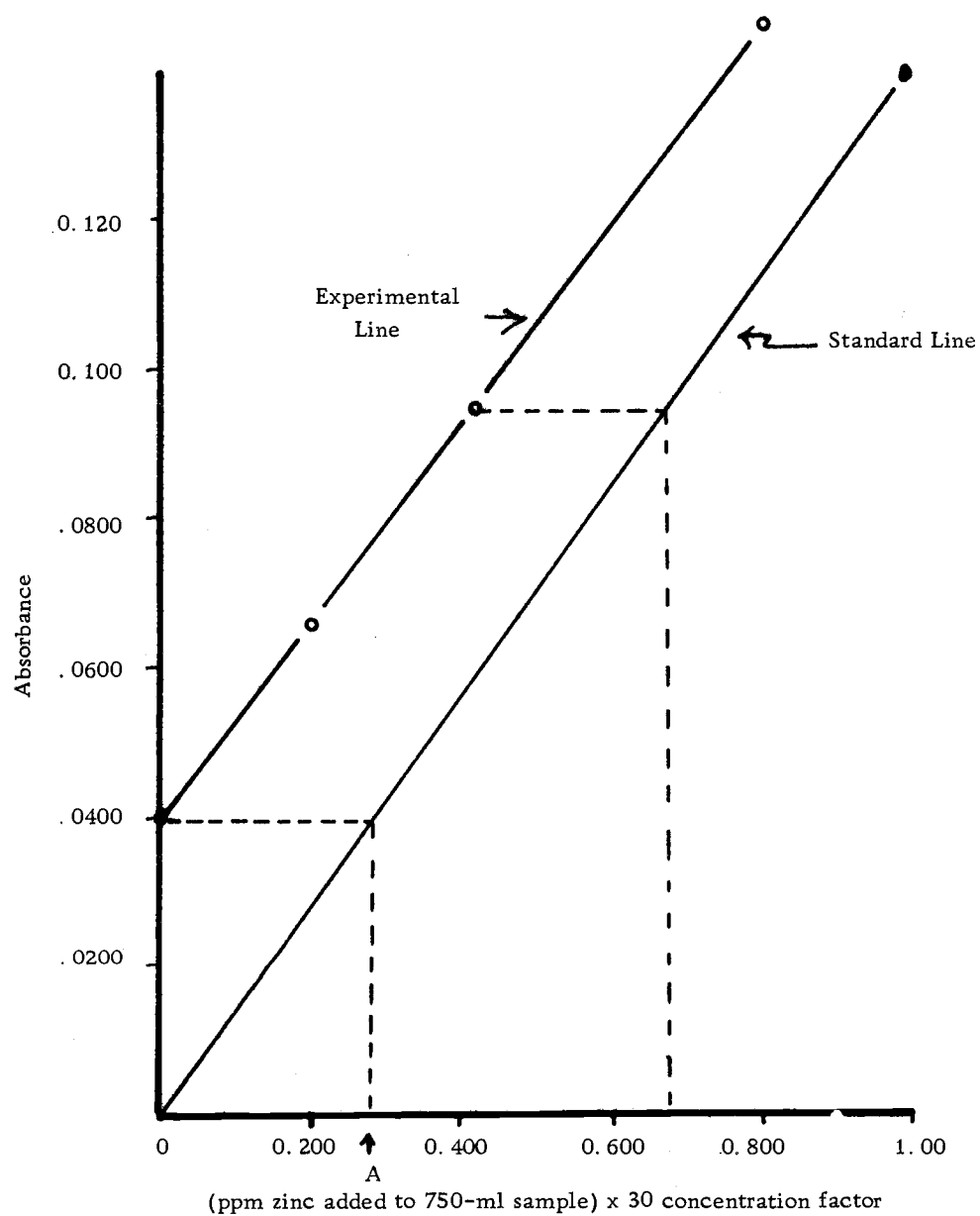
Table 1. Average of weekly observations off Beaufort, North Carolina.

Month	$\mu\text{g}/\text{l}$	Month	$\mu\text{g}/\text{l}$
N	9.7	M	13.2
D	2.8	J	14.1
J	3.5	J	12.4
F	5.4	A	14.6
M	5.0	S	12.1
A	12.1	O	11.6

On one of the cruises made by Fonselius and Koroleff (1963), a complete depth distribution was taken. The maximum zinc value was at 600 meters, coinciding with salinity and temperature maxima at that depth. These samples were taken in the western Mediterranean where the water near the island of Rhodes sinks during the winter to form an intermediate layer. Since the layer originates at the surface, Fonselius believes this may explain the high zinc content.

Method of Additions

Joyner and Finley (1966) used the method of additions approach to the evaluation of recovery. This involves making additions of varying amounts of standard zinc solution to subsamples of sea water, extracting, and plotting the results as absorbance versus ppm of zinc added (See Figure 1). A straight-line relationship indicates consistent recovery of the trace element. This method was employed in this thesis work in the final analysis of the extraction process.



Point A represents the original sea water content (this is a contamination figure if the procedure is applied to distilled-water samples).

Figure 1. Illustration of the method of additions in analysis for zinc in sea water.

EXPERIMENTAL

Sampling

The standard method of sampling for trace metals employs a Van Dorn-type sampler. These have no metal on the interior and are stoppered by rubber plugs. Before using, the two Van Dorn, poly-vinyl chloride units were cleaned thoroughly with concentrated HNO_3 and left overnight with dilute HCl in an effort to free them of contamination. Contamination remained, however, to the extent of about ten parts per billion (ppb) for distilled water stored in the samplers for one hour.

Excluding the Van Dorn sampler, one is left with the plastic bucket for surface sampling or the designing of a new sampler for depths. Fonselius (1963) had a great deal of trouble with ship and sampler contamination of his sea water samples. He turned to an elaborate sampling technique involving attaching 40 meters of nylon wire to the hydrographic metal wire and placing a Van Dorn plexi-glass sampler midway on the nylon wire. An iron weight was used at the end of the nylon wire, and an ordinary Knudsen reversing bottle was attached over the connection point of the two wires. This arrangement allowed for the release of the Van Dorn bottle from the deck via the Knudsen bottle.

Once a sea water sample is brought to the surface, it may be processed as an unfiltered sample or it may be filtered. The time between sampling and processing was kept to a minimum due to possible changes in the zinc content resulting from liberation from or sorption onto particulate matter or container walls. No samples processed at sea should stand longer than one hour before analysis. Even freezing of filtered samples fails to preserve the zinc content of the fresh sample. Riley (1965) suggests that if storage is absolutely necessary, acidifying the solution and storing it in polyethylene is most successful.

Filtering

The need for filtration of sea water samples prior to trace-element analysis has long been recognized. The removal of particulate matter from a sample eliminates the difficult question of "To what extent is the zinc in particulate matter being extracted?" In addition, the use of filtered water allows one to answer more accurately the question being asked, namely, "What is the zinc content of the water?"

The problems inherent in filtering have caused most workers to avoid this step. Filtering may lead to contamination of samples; and if contamination is avoided by using acid-washed filters and holder, loss of zinc by sorption from the sea water onto the filter and/or

holder may occur.

Sea water samples were filtered through a 0.65 μ Gelman filter supported by a sintered-glass disk (Millipore), and drawn into a calibrated vacuum flask. Originally, a glass filter was used as a pre-filter, but this was found to be highly contaminating. Experiments were performed first to establish whether or not loss of zinc occurred during filtration. Results of tracer ^{65}Zn tests showed losses of from 40 to 70 percent, almost entirely due to sorption onto the sintered-glass disk. This variable loss was completely overcome by rinsing ten ml of distilled water through the Gelman filter following filtration, and then removing the filter and passing 25 ml of 0.36 M HCl through the sintered-glass disk. The sea water volume was corrected for these and subsequent dilutions.

Contamination was more difficult to assess. In order to maintain the sample at the normal pH of sea water, NH_3 was added to neutralize the HCl. The NH_3 reagent, however, was not sufficiently pure, resulting in a slight contamination of the filtered samples. For future work, the ammonia should be purified or another base chosen.

The hazard most apparent in filtered samples was random contamination. This could occur at any time, on any given sample. Care had to be taken at all times to ensure clean equipment. This was the most difficult requirement at sea. The cleaning process

consisted of washing with concentrated nitric acid and a thorough rinsing with distilled water. If significant amounts of organic matter were involved, a thorough wash with acetone and distilled water preceded the acid wash. A more quantitative look at contamination will be given later.

Liquid Extraction

Initial Work

The working procedure which initiated the present investigation was described by Cronin (1965). The method consisted of filtering 500 ml of sea water through a $0.45\ \mu$ glass membrane filter and buffering to a pH of 6.8-7.0 using 0.5 M citric acid buffer. Following the addition of two milliliters of two percent chelating agent (sodium diethyldithiocarbamate), the sea water was shaken periodically for one hour, and the chelated zinc was extracted into the organic solvent methylisobutyl ketone (MIBK). This was shaken for another half hour and separated. Analysis on the Perkin-Elmer Model 303 Atomic Absorption Spectrometer completed the determination.

Although results were satisfactory in the laboratory, variable results were obtained on samples processed at sea. The first modification of this procedure was the mechanization of the mixing and the standardization of the timing so that results would be

independent of personnel. A shaking machine with a timing device was modified to handle eight 1000-ml separatory funnels (Figure 2).

Zinc-65 tracers were used initially to follow the steps in the extraction process and to evaluate the extent of extraction. A known amount of zinc-65 was transferred quantitatively to 500 ml of sea water in a separatory funnel. The extraction procedure as described above (minus the filtering) was then carried out with the exception that the organic layer was drained into a volumetric flask and diluted to 100 ml. Percent recovery was determined on a five-ml aliquot by gamma ray spectrometry. In the laboratory the organic extraction process gave a recovery of $97 \pm 2\%$, but was found inadequate for shipboard use due to the instability of the extracted sample. This instability was evidenced by drastic reductions in the recoveries of aliquots taken later from the original extract. Apparently absorption onto the container walls was responsible as indicated by the increased count rate with time of a given sample in a given counting tube. The increased rate was due to the changing geometry within the tube brought about by adsorption onto the walls of the tube.

A back-extraction into HCl was then attempted and proved to be highly successful. The solution was stable within counting statistics for a period of three weeks, and an additional concentration factor of four was attained. A much higher concentration factor is possible on the back-extraction.

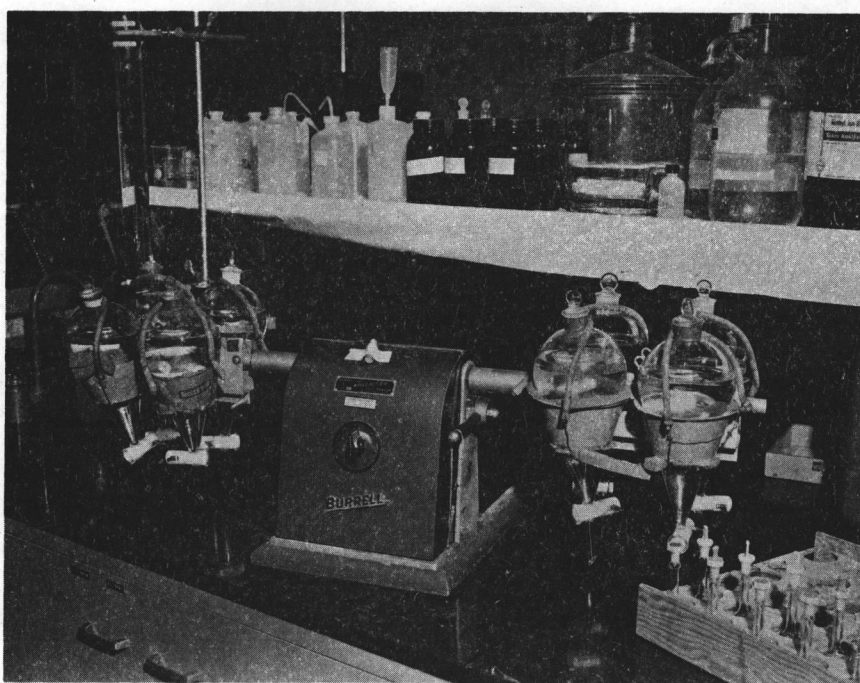


Figure 2. Wrist-action machine modified to handle 1000-ml separatory funnels.

Method of Analysis by Liquid Extraction

The extraction procedure was studied to determine the minimum time required for shaking and reagent volumes needed for successful extraction. Following is the procedure in its final form: Measure carefully 750 ml of sea water into a 1000-ml separatory funnel. Chelate with two milliliters of two percent NaDEDTC and add 100 ml of MIBK. Shake for 60 minutes. Drain off the lower aqueous layer and add 200 ml of 0.36 M HCl to the organic phase in the separatory funnel and shake for 20 minutes. Since some of the MIBK will have dissolved into the aqueous phase, drain the HCl layer into a 25-ml volumetric flask and dilute to the mark. In this way a known concentration factor of 30-fold is realized.

Experiments to determine whether the extraction could be carried out at the normal pH of sea water showed the procedure to be equally efficient at the sea water pH of about 8.01 as at the buffered pH of 6.8-7.0.

Recovery

In the early tracer studies, five-ml aliquots were analyzed in a multichannel analyzer for recovery of zinc-65 spike. These yielded a recovery of $97 \pm 2\%$. Later, when unspiked replicate sea

water samples were extracted and analyzed on the AAS, reproducibility was good (Table 2). These simultaneously-run duplicate samples gave a standard deviation of 1.2%, all four samples falling within 1.2 standard deviations.

Table 2. Replicate sea water samples analyzed on the AAS.

sample	ppm [*]
a	2.78
b	2.73
c	2.72
d	<u>2.79</u>
average	2.76 ± 0.04

* These samples are abnormally high in zinc content due to filtration through a zinc disk.

Experiments at Sea

At this point the process was taken to sea to check equipment, personnel, and sample storage possibilities. Sampling was done with a three-gallon PVC-formica Van Dorn bottle and analysis followed immediately. Duplicate samples were kept in polyethylene bottles for periodic sampling back at the lab. These results are shown in Table 3.

Table 3. Zinc in ppb of sea water from four collections (four sub-samples of each).

sample	location	1st run (4/12-4/14)	2nd run (4/20)	3rd run (5/17)
		ppb Zn	ppb Zn	ppb Zn
1. a	NH 15	39.0	72.0	69.4
b	surface	46.7	71.4	69.4
c		52.7		
d		<u>60.7</u>	_____	_____
	average =	49.8	71.7	69.4
2. a	NH 65	54.0	80.0	82.6
b	surface	52.7	80.0	80.4
c		41.0		
d		<u>45.4</u>	_____	_____
	average =	48.3	80.0	81.5
3. a	NH 65	14.0	23.0	20.7
b	100 m.	14.0	23.0	20.7
c		15.8		
d		<u>16.0</u>	_____	_____
	average =	15.0	23.0	20.7
4. a	NH 65	14.0	13.0	16.3
b	300 m.	13.3	16.0	16.3
c		15.3		
d		<u>16.7</u>	_____	_____
	average =	14.8	14.5	16.3

These results are evidence of the need for shipboard extraction. With time, three of the samples increased up to 70 percent in extracted zinc. An investigation into the effect of a one-day interval was made in Astoria. A large sample of sea water was filtered and divided into two aliquots. One aliquot was run at the dock while the other was returned to the lab and processed the following day. Care was taken to avoid contamination between the first and second runs (Table 4). The difference in the first samples may or may not be real. This is a question that often occurred. Since the samples were filtered, the water would be expected to be fairly well mixed, and one is then faced with a possible nine percent difference in the duplicate analyses. The results of the experiment are clear, nevertheless. A one-day wait shows an increase of 50 percent over the fresh sample analyses.

Table 4. Zinc content (ppb) of a sea water source sampled when fresh and after a one-day interval.

sample	ppb
#1-run at dock	29
(duplicates)	<u>32</u>
average =	30
#2-one day later	45
(duplicates)	<u>46</u>
average =	46

Introduction of Filtering

The wide spread in the surface values of the first run of Table 3 prompted the introduction of filtering to the procedure. It was felt that particulate matter might well be responsible for variation since the surface samples, which are high in particulate matter, showed greater variation than the deep samples, which were low in particulate matter.

With filtration, full evaluation of the procedure required not only a percent yield and a variation factor, but also a close examination of contamination. Not only can additional reagent contamination be introduced by filtering, but the mere addition of another step in the procedure can lead to random contamination by sample handling.

Analysis by Method of Additions Using Distilled Water

An approach to evaluation of the process other than by replicate samples was begun at this point. Use was made of stable-zinc standards and the method of additions described in the Introduction.

The method of additions was applied to both distilled water and sea water. Only the actual extraction process was tested. To test whether or not analogies could be made between distilled water and sea water experiments, known amounts of zinc-65 were added to 750-ml of both distilled water and sea water (Table 5). The percent

recovery of the spike was the same for both media, implying a similar behavior of zinc-65 in sea water and distilled water.

Table 5. Extracted sea water and distilled water samples spiked with ^{65}Zn .

sample	(cpm) standard	(cpm) HCl recovery	% recovery
sea water	311,000	293,400	95.3
sea water	315,400	304,700	96.6
sea water	317,800	308,200	97.0
distilled water	309,000	309,000	96.6

The method of additions was first applied to distilled water. In this way, the total zinc (μg) extracted would be comparable to that obtained from sea water extractions. Distilled water runs also gave information on contamination. A total of three complete runs were made (Figures 3, 4 and 5). The lines drawn through the experimental points were determined by the method of least squares. The determination of the percent recovery in these three cases could be made by a simple comparison of the experimental slopes with the standard slopes. On the sea water runs, the experimental least squares fit overlaps more than one straight line segment of the standard curve (Figure 7), and a simple comparison of slopes is not

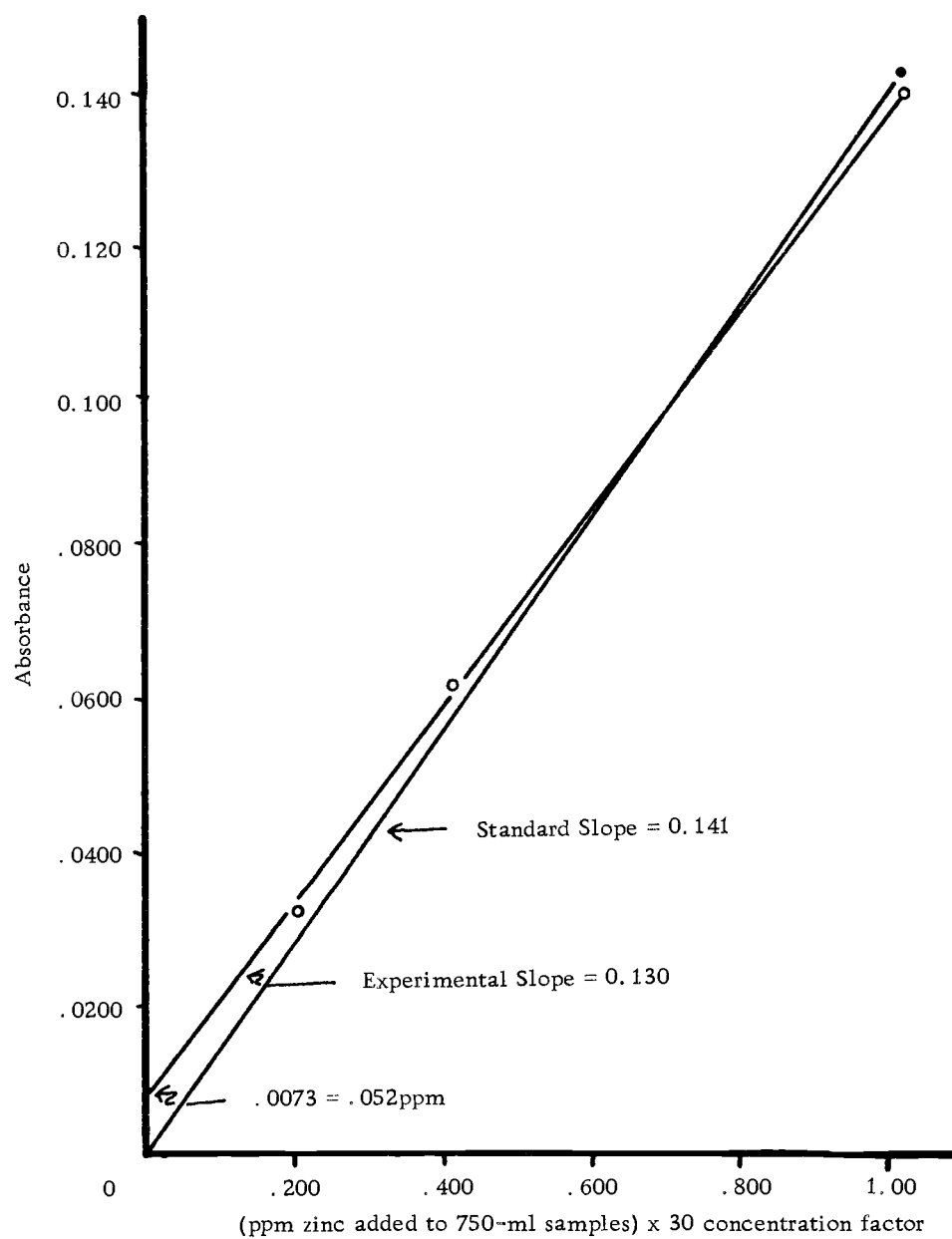


Figure 3. Method of additions applied to distilled water-- first trial.

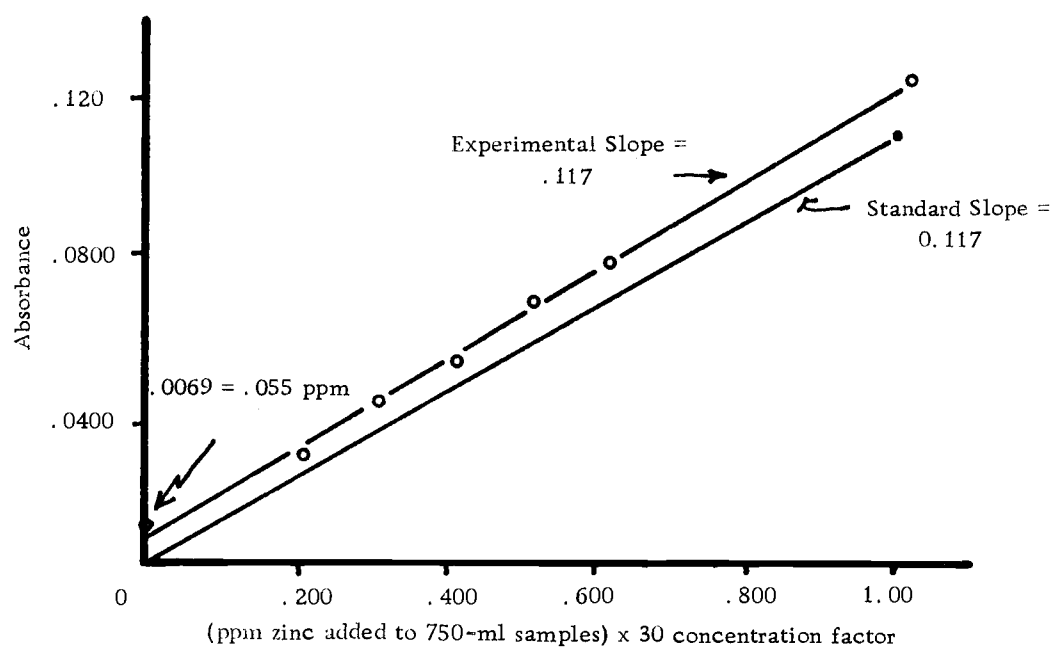


Figure 4. Method of additions applied to distilled water--second trial.

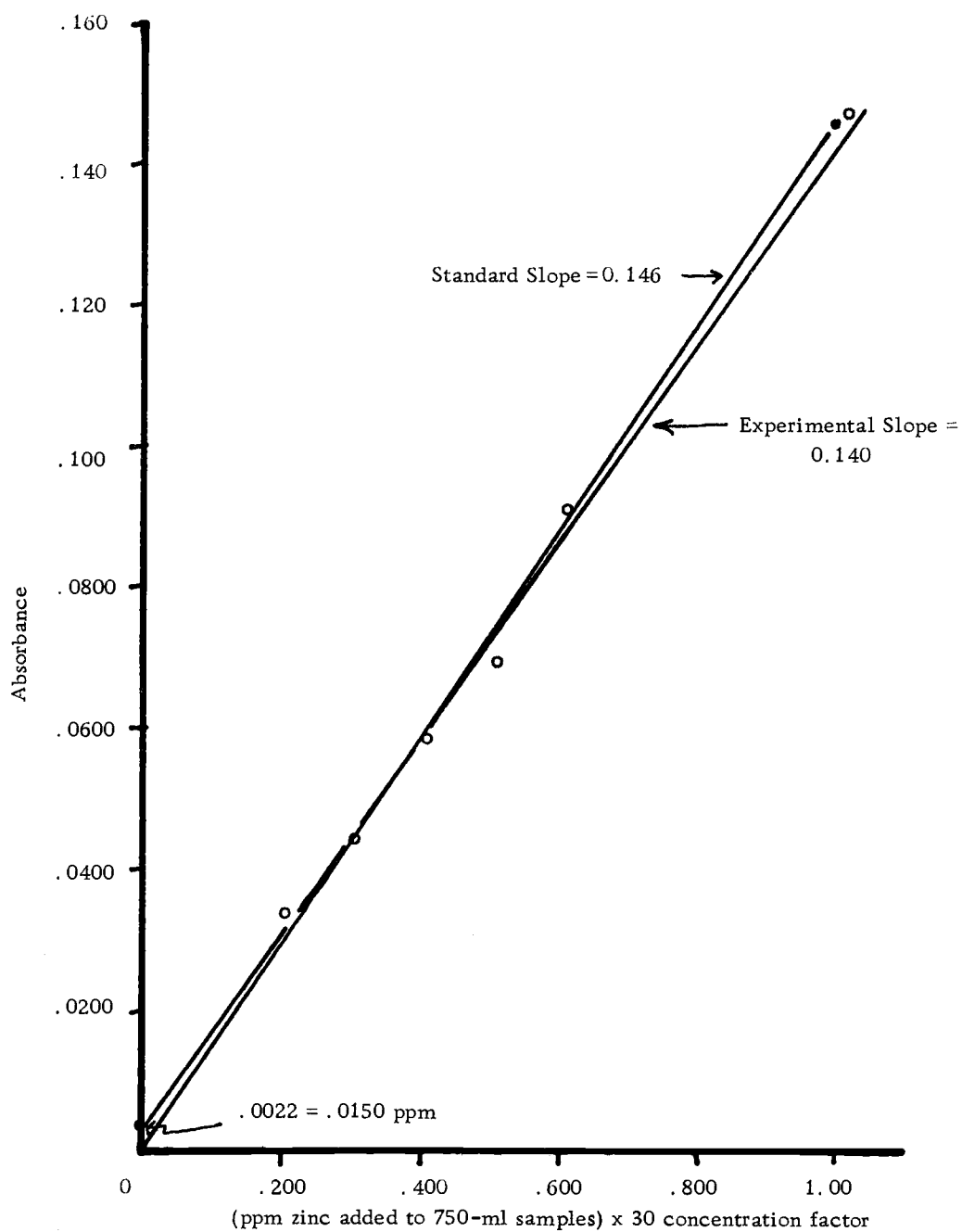


Figure 5. Method of additions applied to distilled water--third trial.

feasible. The method used instead was to take the intercept value A, convert it to ppm from the standard curve, and subtract this value in ppm from each experimental value in ppm. The resulting difference is compared with the amount of stable zinc added, and the percent recovery is calculated (see Table 6).

Table 6. Sample calculation using data from Figure 5.

sample	A	ppm	ppm minus intercept	ppm added	% recovery	$\bar{x} - \bar{x}$	$\sqrt{\frac{\sum (x - \bar{x})^2}{n-1}} = \text{std. dev.}$
#1 Std.	.1494	1.02					
#2 Std.	.2976	2.04					
a	.0031	.021	.006	0	--	--	
b	.0339	.231	.216	.204	106	9	
c	.0443	.302	.287	.307	93.5	3.1	
d	.0585	.399	.384	.409	93.9	2.7	
e	.0691	.472	.457	.511	89.4	7.2	
f	.0910	.621	.606	.614	98.7	2.1	
g	.1475	1.01	.99	1.02	96.9	0.3	
h	.2916	2.01	1.99	2.04	97.5	0.9	
					96.6%		
					(average)		$\pm 5.1\%$

Figure 3 represents the first trial using the method of additions. To all appearances, it was a mechanically good run. But with only three points and the omission of a zero-addition point, the intercept value may well be high. The hidden curve within these points would slope more strongly between the zero-addition and first-addition point and serve to increase the slope of the line. This would decrease the intercept value and increase the calculated recovery.

Figure 4 represents a run which was not mechanically good. Large numbers of bubbles were present at the interface of the distilled water-MIBK layers during the initial extraction step. Bubbles were a problem on distilled water runs generally, and care had to be taken that no surface-active agents were used even in the initial steps of cleaning the glassware, unless excessive care was taken to give thorough and repeated rinsings with acid and distilled water.

The run illustrated in Figure 5 appeared to be an excellent mechanical run with a good range of values. The fluctuation of percent recoveries around the mean is greater in this run than in the previous two, but this may be more realistic. A sample calculation of the data for Figure 5 is given in Table 6. Unless stated otherwise, similar calculations applied to all subsequent data.

The results of the calculations for the data of Figures 3, 4, and 5 are given in Table 7. The recoveries found by a simple comparison of experimental and standard slopes is included for comparison.

Table 7. Recoveries calculated from the data of Figures 3, 4 and 5.

figure	% recovery, std. dev.	exp. slope/std. slope	intercept (ppm)
3	92.3 \pm 3.5%	92.2%	.025 (.052)
4	97.2 \pm 2.8%	100 %	.059
5	96.6 \pm 5.1%	95.9%	.015 (.021)

The intercept given for Figure 3 was derived from a line drawn through the first two experimental points and through the y-axis. This more accurately defines the actual intercept than does a line through all three points. The latter intercept is indicated in parenthesis. The number in parenthesis for Figure 5 is the actual experimental point. These factors will be needed in the determination of the contamination for the procedure.

It should be stressed at this point that the numbers given on the graphs and in the tables are for the concentrated (30x) samples. Thus, the contamination of .021 ppm in the experimental, zero-addition point of Figure 5 is the equivalent of .021 ppm/30 or 0.7 ppb contamination--or uncertainty--in the original water sample.

Analysis by Method of Additions Using Sea Water

Three runs were made later using sea water. The total recovery in these experiments was much higher than the actual sea

water samples, however, since additions of up to one ppm were made. In addition, the sea water used was unusually high in zinc, having been either filtered through a sintered-zinc disk or stored for some time. The procedure and recovery were nonetheless valid, though the ordinate intercept indicating the sea water content was not representative of in situ water.

Prior to this time, the calibration standards were made with distilled water. Use of standards of HCl saturated with MIBK was now begun to duplicate the composition of the extracted sample. There was only a slight difference between the standards in the range from zero to one ppm (Figure 6). The difference increased with increasing ppm but this higher range was not used in the analysis of the procedure.

Figures 7 and 8 show the sea water runs made using the method of additions. Table 8 shows the calculations for runs 7a, 7b and 7a + 7b. Table 9 summarizes the results of calculations on these three sets of points:

Table 9. Results of three sea water runs using the method of additions.

sample	% recovery	recovery of 7a and 7b combined
7a-filtered	99 \pm 1	
7b-unfiltered	95 \pm 7.6	97 \pm 5.4%
8-filtered	95 (median)	

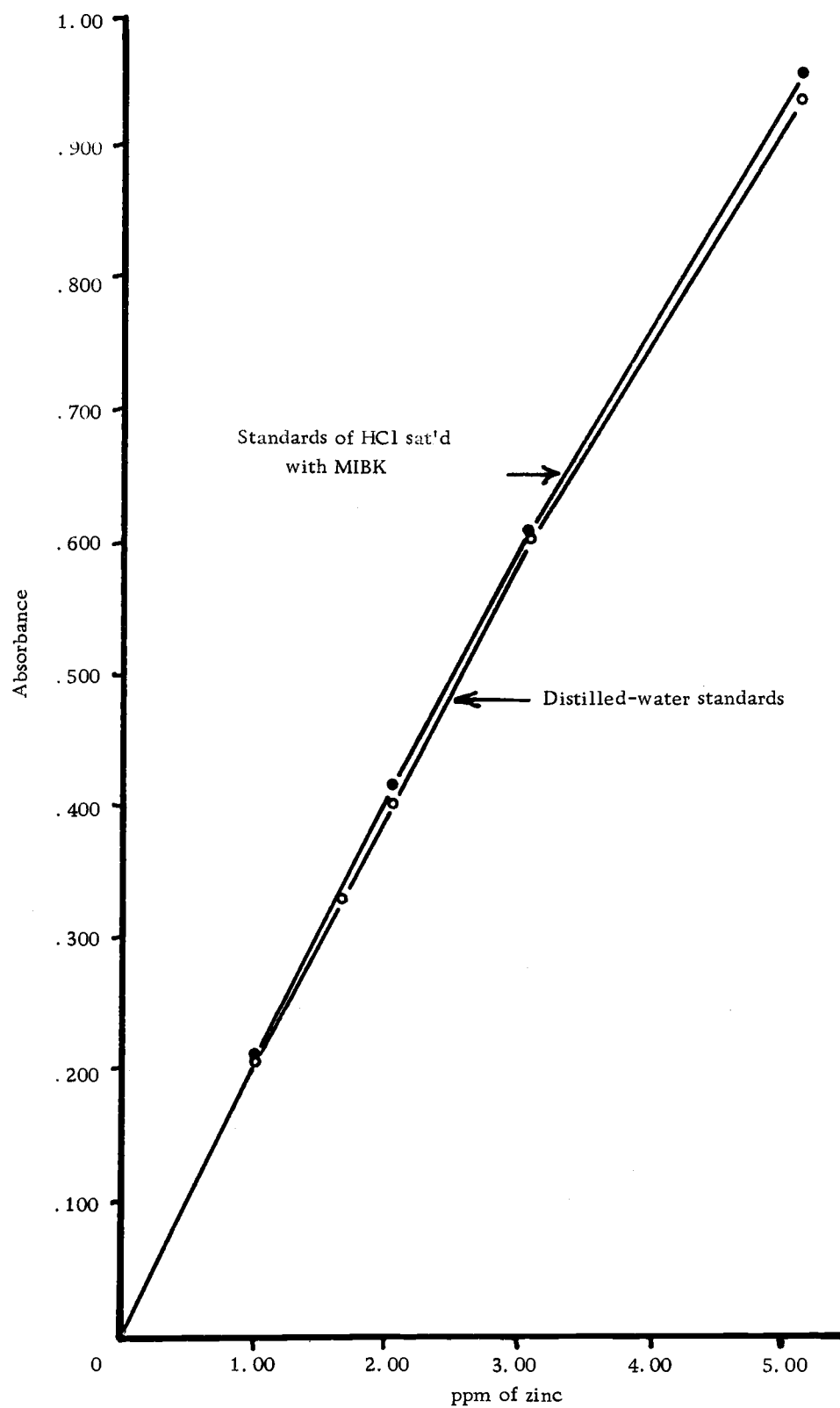


Figure 6. Standard curves of zinc absorbance vs. concentration in distilled water and in HCl saturated with MIBK.

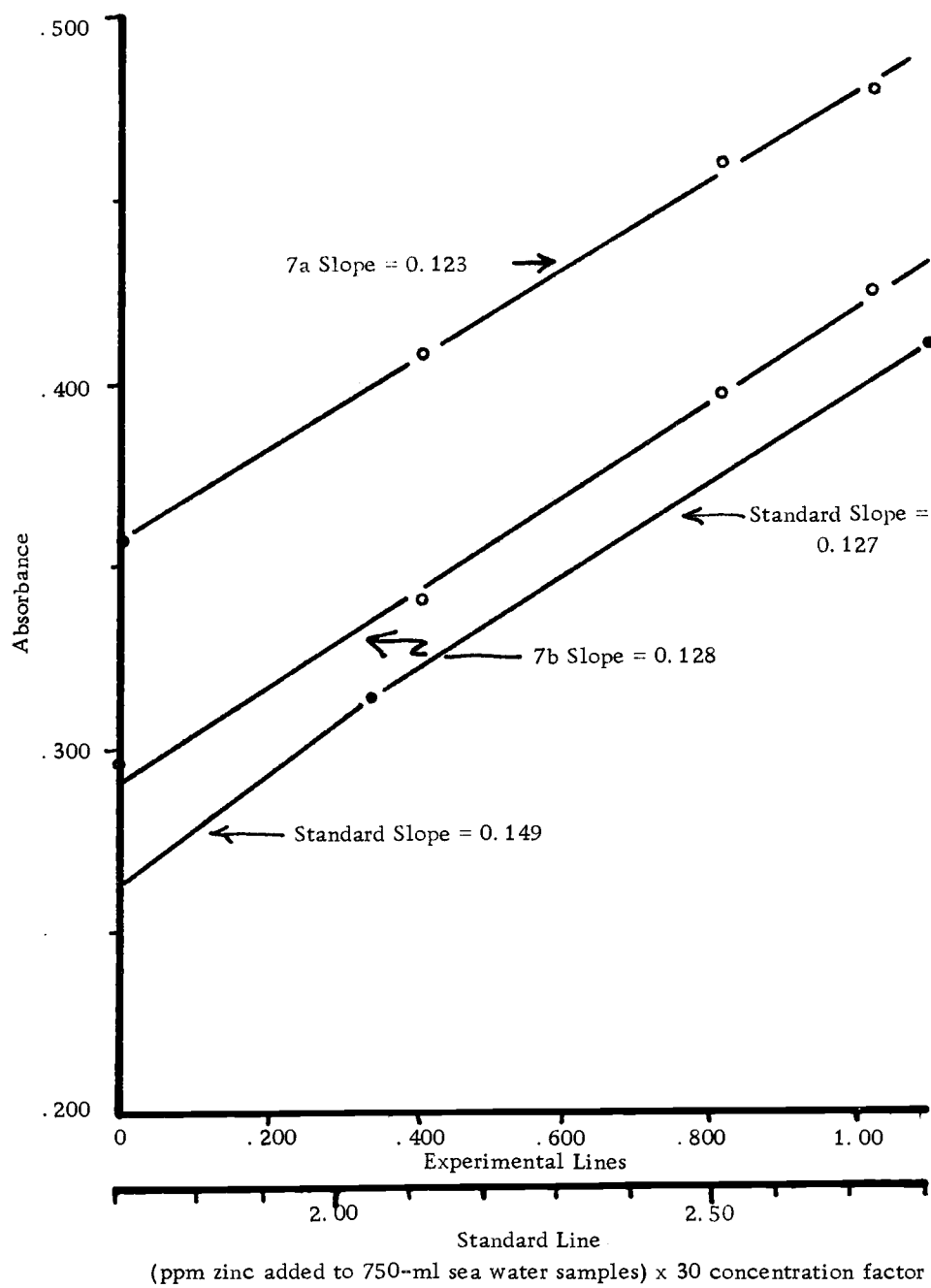


Figure 7. Absorbance values of sea water samples analyzed by the method of additions.

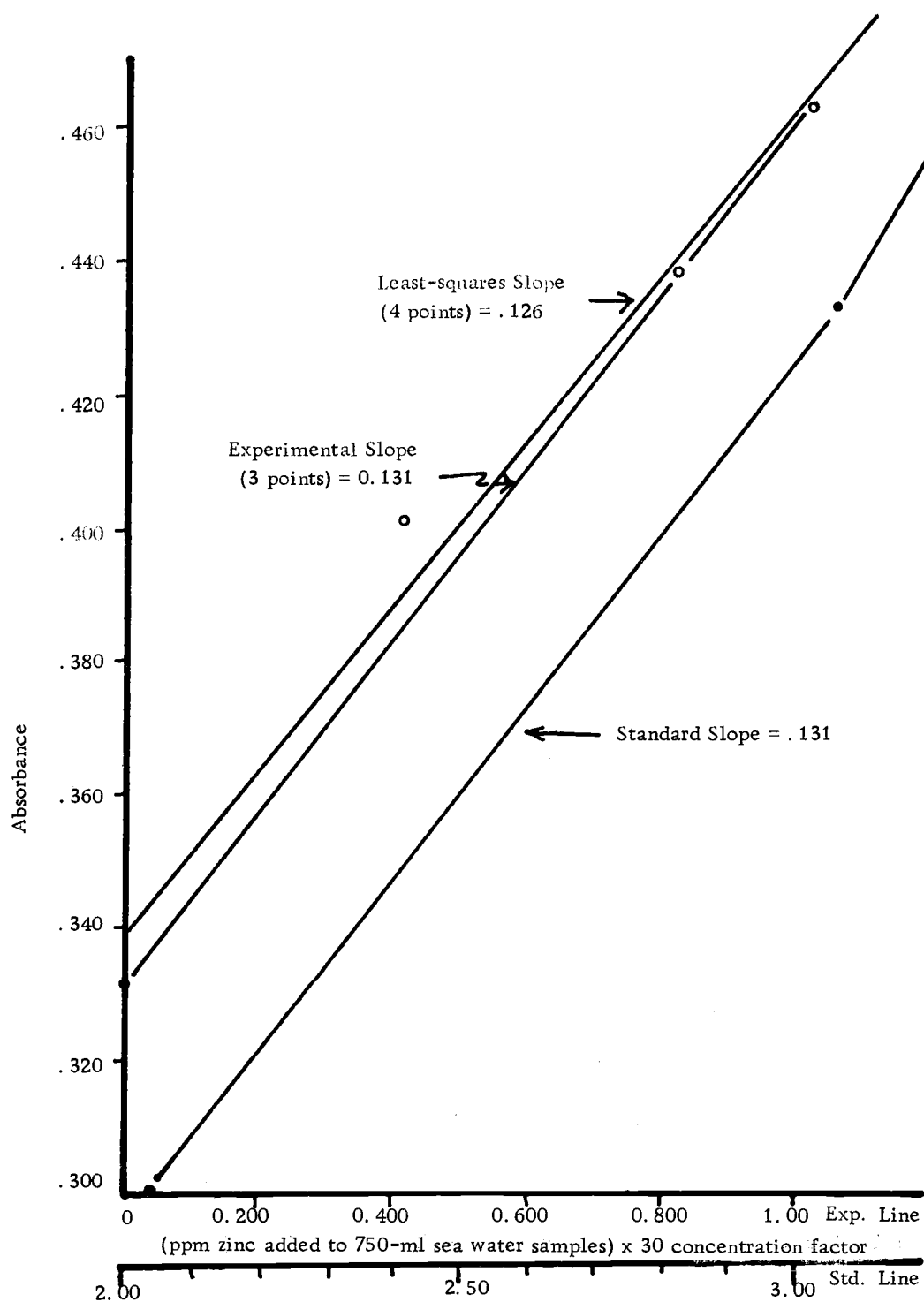


Figure 8. Sea-water samples analyzed by the method of additions. These data illustrate the least-squares fit using all four points vs. the use of only three of the four experimental points.

Table 8. Calculations on the data from Figure 7.

sample	A	ppm	ppm minus intercept (2.38)	ppm added	% recovery	$\bar{x} - x$	$\sqrt{\frac{\sum (x - \bar{x})^2}{n-1}} = \text{std. dev.}$
#1 Std.	.1624	1.02					
#2 Std.	.3143	2.04					
#3 Std.	.4437	3.06					
#4 Std.	.5607	4.08					
7a 1	.3566	2.37	-.01	0	--	--	
2	.4089	2.78	.40	.409	98	1	
3	.4609	3.21	.83	.818	100	1	
4	.4815	3.39	1.01	1.02	99	0	
average =					99%		± 1
			(intercept = 1.90)				
7b 1	.2958	1.92	.02	0	--	--	
2	.3410	2.25	.35	.409	86	9	
3	.3979	2.70	.80	.818	98	3	
4	.4260	2.92	1.02	1.02	100	5	
average =					95%		± 7.6
overall average =					97%		$\pm 5.4\%$

These three runs were mechanically good, yielding further information on the percent recovery in sea water. The combined 7a and 7b value is included since these runs were made simultaneously from different sample sources. 7a was a filtered source whereas 7b was unfiltered.

Incidental, or spot contamination occurred in run 8. Rather than deciding whether or not to throw out the second value (Table 10), the median value (as recommended by Dean and Dixon, 1951) of the three individual percent-recovery figures was taken.

Table 10. Recovery figures for data in Figure 8.

sample	percent recovery
a	---
b	120
c	95 --median value chosen
d	93

Contamination

Aside from incidental or spot contamination, the presence of any reagent contamination or general contamination which could be quantified was investigated more fully.

Replicate extractions made on distilled water samples with no

standard-zinc spike added gave the results shown in Table 11. The first six listed samples tested all but the filtration contamination, i. e. they tested the extraction process alone. A simple average of the six yields .008 ppm contamination of the concentrated samples. The range of contamination was from 0 to 0.025 ppm.

Table 11. Extractions performed to test for contamination.

sample	description	ppm
a	distilled water--no filtration	0
b	"	0
c	"	0
d	"	0
#3	(intercept from Figure 3)	.025
#5	(zero-addition point from Figure 5)	<u>.021</u>
	av. =	.008
e	distilled water passed through filter setup--no filtration	0
f	reagent used.	<u>.084</u>
	av. =	.042
g	distilled water plus filter reagents--not actually	.044
h	filtered.	<u>.015</u>
	av. =	.030

The possibility of contamination resulting from the filtration procedure was investigated with samples e through h. The results of groups a, b, c, d, 3, 5 and e, f, g, h are somewhat additive since they test two separate aspects of the filtration, namely contamination

due to filtration reagents, and contamination due to glassware and sample handling. One or both, however, might include a contamination from the actual extraction, and thus the total of the two is a maximum figure of contamination for the entire procedure. This total is 0.072 ppm in the concentrated sample or its equivalent of 2.4 ppb contamination of the original sample. It is possible, however, that if HCl had been used in the filtration process in e and f (Table 11) there would have been a greater contamination effect (despite the fact that the filter apparatus was washed thoroughly with HCl prior to use).

Two sets of experiments were designed to detect contamination in sea water and spiked distilled water samples carried through the entire (filtering plus extraction) procedure. For the first set of experiments, a sample from a large source of sea water was placed in a separatory funnel. The remaining sea water was filtered and part of this was placed in a second funnel. The remaining filtered sea water was then refiltered, sampled, and filtered a third time and again sampled, with the results shown in Table 12.

The second set of experiments was performed on distilled water spiked with stable zinc. A portion (750 ml) was placed in a separatory funnel for direct extraction. The remainder was filtered before analysis (Table 13).

Table 12. Results of sea water filtered and refiltered three times.

sample	ppb Zn (in original sea water)
unfiltered	65.0
filtered once	62.9
filtered twice	63.5
filtered thrice	<u>68.1</u>
	64.9 \pm 2.3% (std. dev.)

Table 13. Filtered and unfiltered samples from the same spiked (stable zinc) distilled water source.

sample	ppm
unfiltered	1.19
filtered	1.19

In both sets of experiments, possible contamination is concealed by the abnormally high zinc levels present in the samples.

Sea Water Values--Plots

The contamination problem with the Van Dorn samplers was discussed under SAMPLING. The Van Dorn samplers were used, however, on a ten-day cruise taken on the R/V Yaquina. The plume of the Columbia River was followed from a point 250 miles west of Newport, Oregon to a point west of San Fransisco. These values are tabulated (Table 14) to give an indication of the range of concentrations found.

The unfiltered samples are the more precise. Filtered surface samples give an average of 24 ppb zinc whereas unfiltered surface samples average 17 ppb. The overall average of surface samples yields 21 ppb zinc. The average sample values decrease with depth to 7.05 ppb at 300 meters. A leveling-off effect is seen in the 50-100 meter range with about ten ppb. The locations and depth distributions of the values are shown in Figures 9 through 13.

Table 14. Data taken on R/V Yaquina, August 1966.

Station	Position		Date	T.O.A.	Sfc	10m	20m	ppb Zn*			
	Lat.	Long.						50m	100m	150m	300m
WG 5	44° 39.1 N	129° 53.2 W	8/17	1800	44.4	<u>21.3</u>					
WG 6	44° 02.5	129° 02.3	8/18	0315	10.9	19.8					
WG 7	43° 28.0	128° 14.0		0812	14.1	9.94					
WG 8	43° 07.2	127° 46.2		1139	18.9	14.2					
WG 10	42° 32.0	126° 58.0		1706	21.2	22.5					
WG 12	41° 58.0	126° 10.5		2310	15.5	11.7					
WG 14	41° 21.0	125° 23.0	8/19	0440	23.6	49.2					
WG 16	40° 53.8	124° 50.0		0858	13.2	10.6					
WG 17	40° 17.0	125° 32.0		1621	15.4	12.8					
WG 18	39° 41.5	126° 12.7		2142	20.8	21.0					
WG 19	39° 06.0	127° 03.6	8/20	0300	27.8	17.6					
WG 20	38° 30.0	127° 47.0		0800	34.5	18.4					
WG 21	37° 53.8	128° 32.5		1320	<u>10.2**</u>	5.62	6.17	6.36			
WG 22	37° 18.0	129° 20.0		2302	11.0	12.7	14.0	19.9			
WG 23	37° 20.0	128° 16.8	8/21	0800	(23.4)		18.8	7.86	10.9		
WG 24	38° 08.9	128° 02.0		1440	14.2		8.14	14.9	<u>5.05</u>		
WG 26	39° 46.0	127° 43.8	8/22	1008	19.0		29.9	14.4	<u>16.5</u>		
WG 27	40° 37.0	127° 28.5		1610	23.2		9.18	6.87	<u>9.43</u>		
WG 28	41° 26.2	127° 17.0		2155	16.6		6.52	5.90	<u>6.05</u>		
WG 29	42° 15.2	127° 06.0	8/23	0605	39.4		9.12	6.66	<u>13.5</u>		
WG 30	43° 03.9	126° 51.9		1135	9.14		7.10	<u>4.52</u>			<u>6.90</u>
WG 31	43° 53.0	126° 39.0		1650	9.30		3.87	11.8		<u>4.71</u>	<u>7.20</u>
WG 32	45° 17.9	124° 01.8	8/24	1500	11.6		14.5				
WG 33	45° 17.4	124° 19.8	8/24	2030				14.6		12.4	
WG 34	44° 42	125° 34.3	8/25	1200	22.8		12.7	5.64		5.83	
average:					20.6	17.8	11.6	10.1	10.2	7.65	7.05

* Runs WG 5 through WG 20 were filtered prior to analysis. Runs WG 21 through WG 34 were not filtered.

** Underlined values represent a single determination for that point. All other ppb Zn values are the average of duplicate runs.

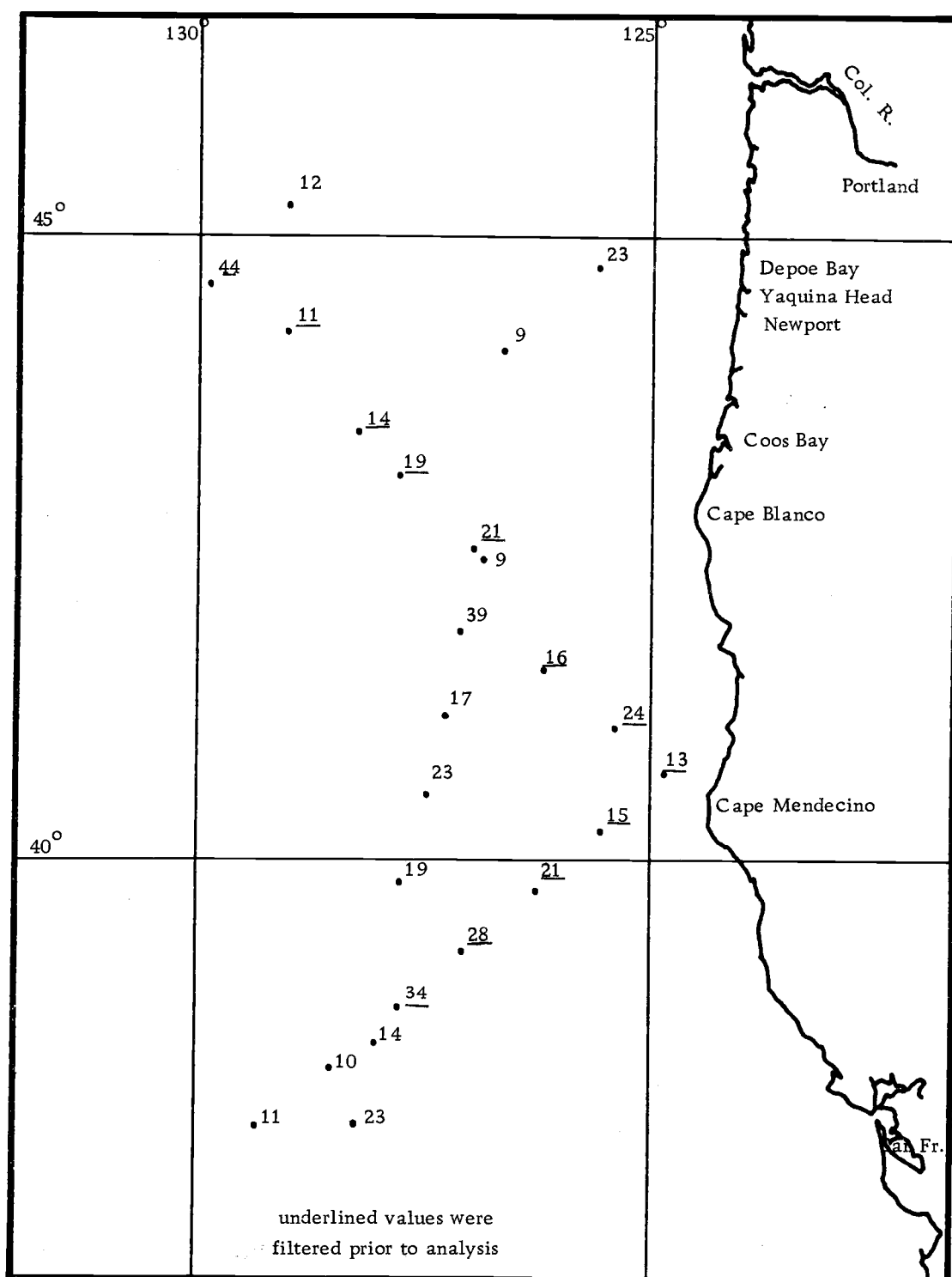


Figure 9. Surface values of zinc (ppb) from "WG" cruise, August 1966.

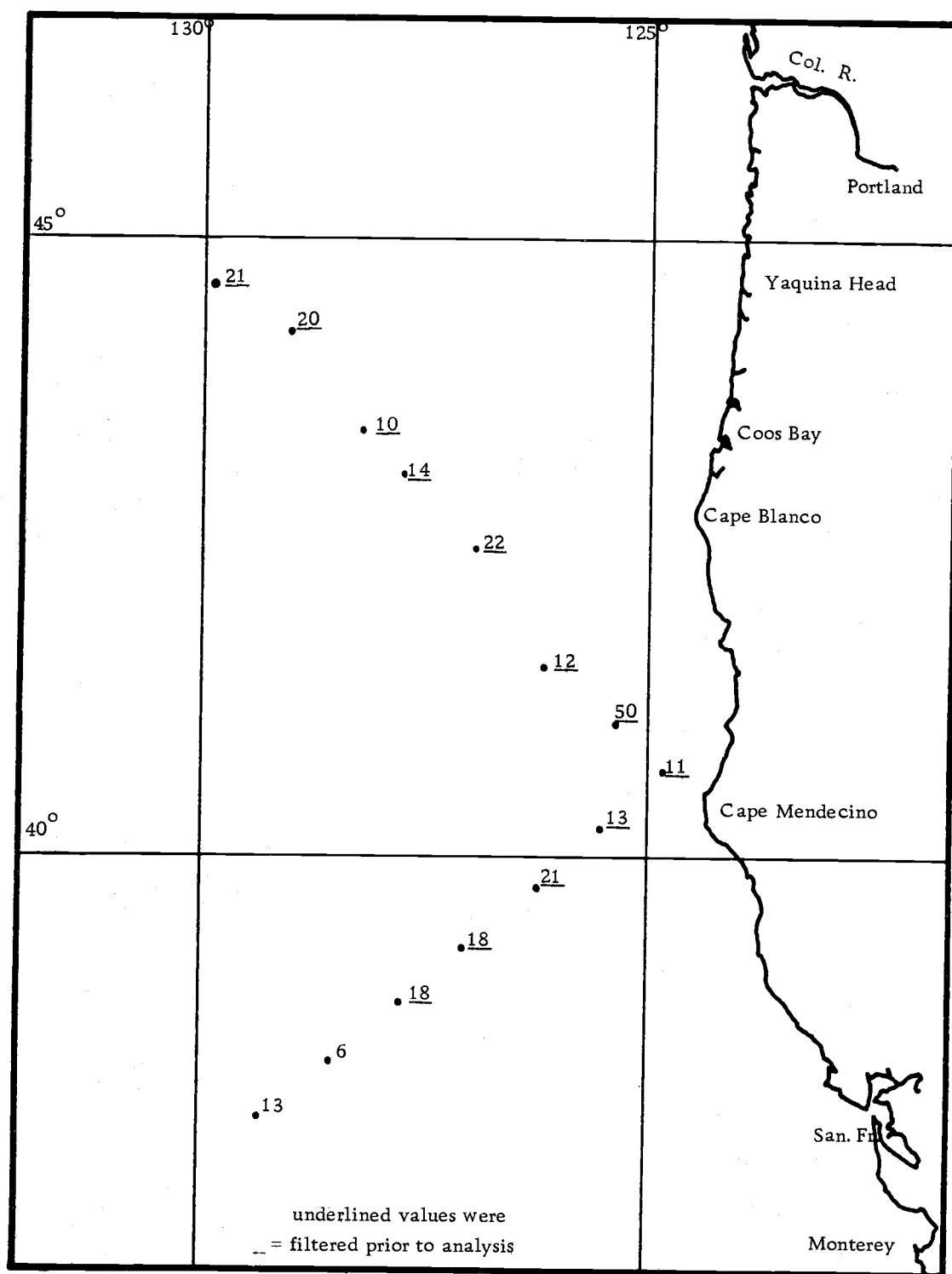


Figure 10. Values of zinc (ppb) at a depth of ten meters from "WG" cruise, August 1966.

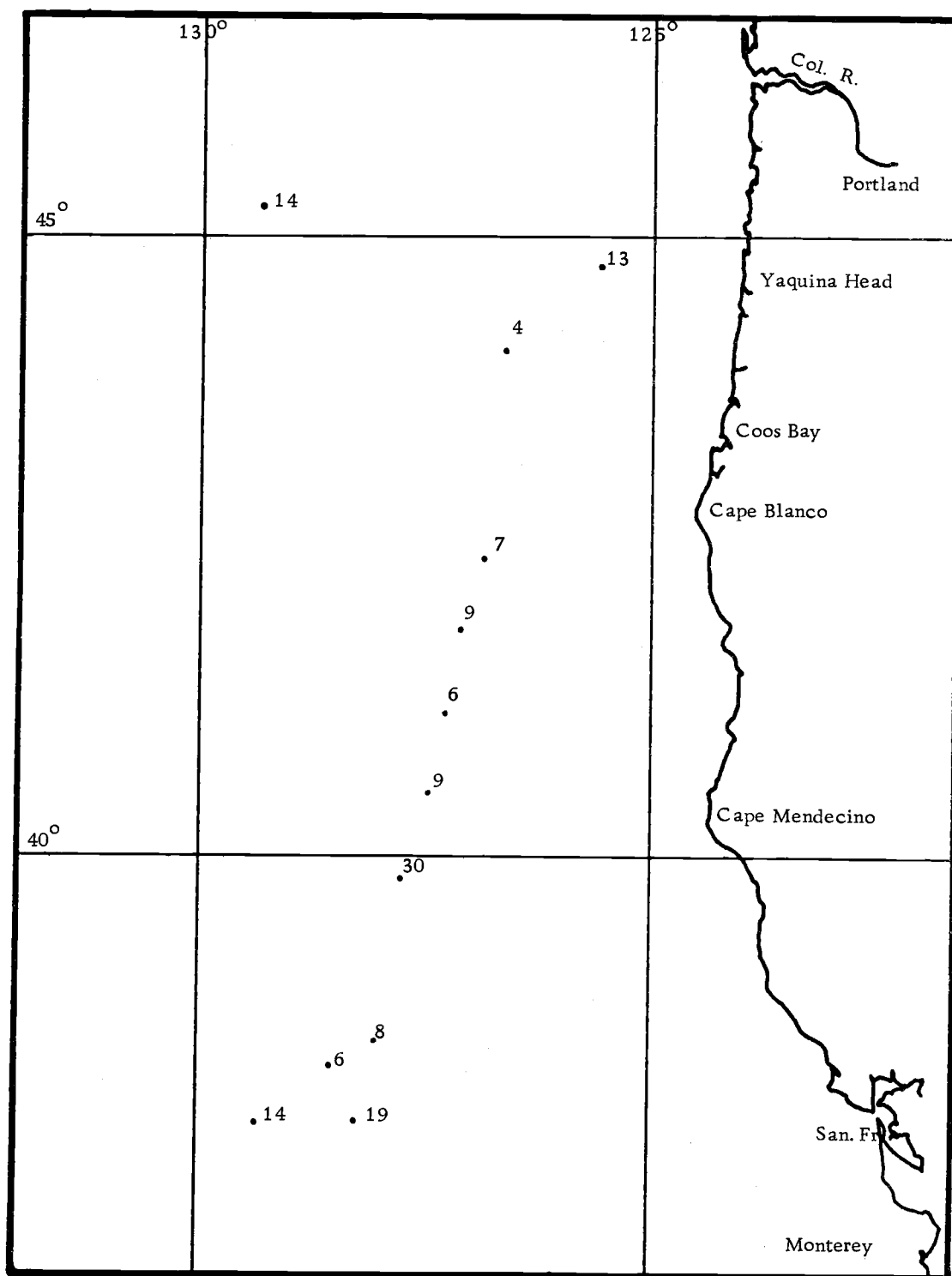


Figure 11. Values of zinc (ppb) at a depth of twenty meters from "WG" cruise, August 1966.

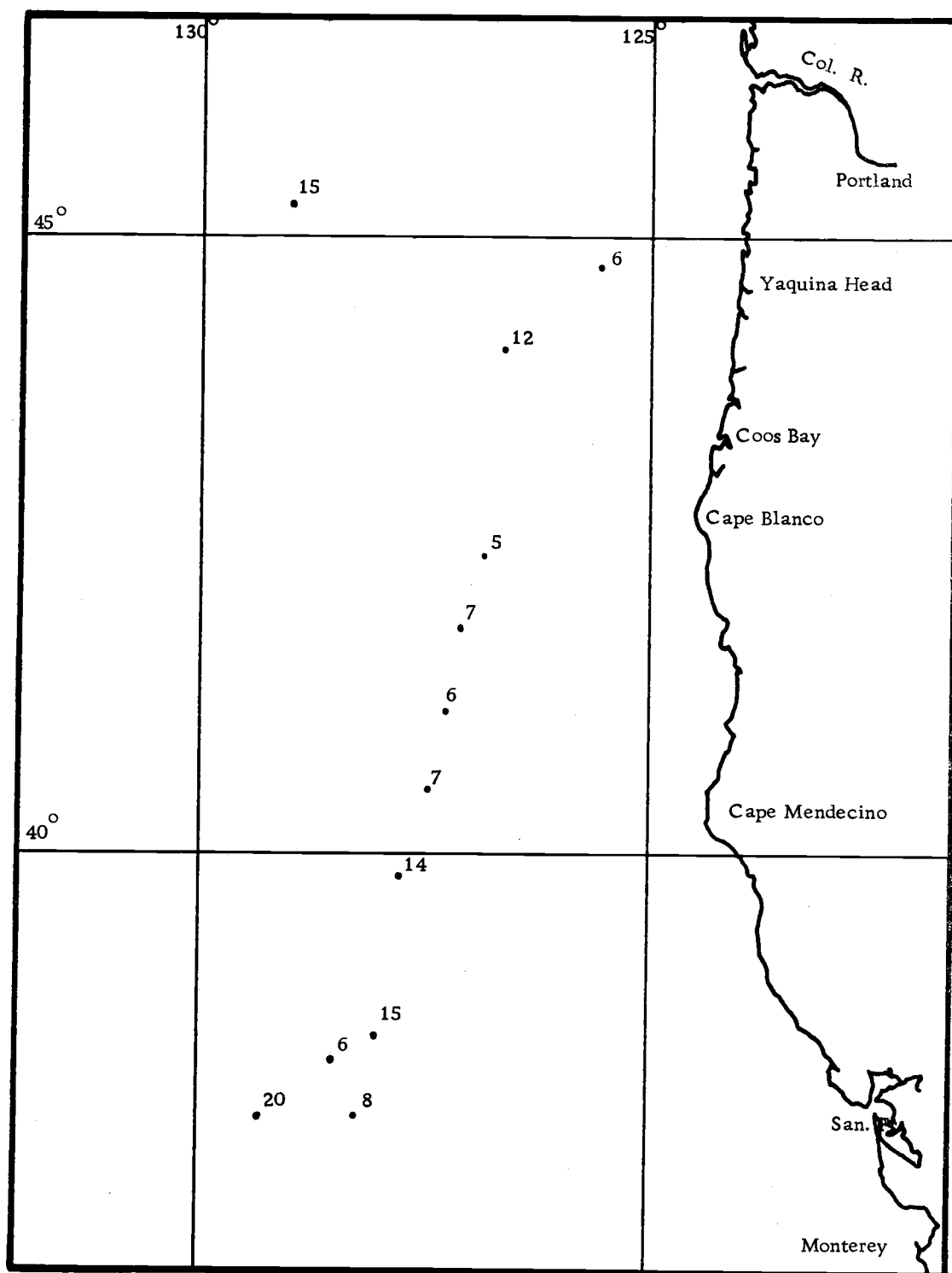


Figure 12. Values of zinc (ppb) at a depth of fifty meters from "WG" cruise, August 1966.

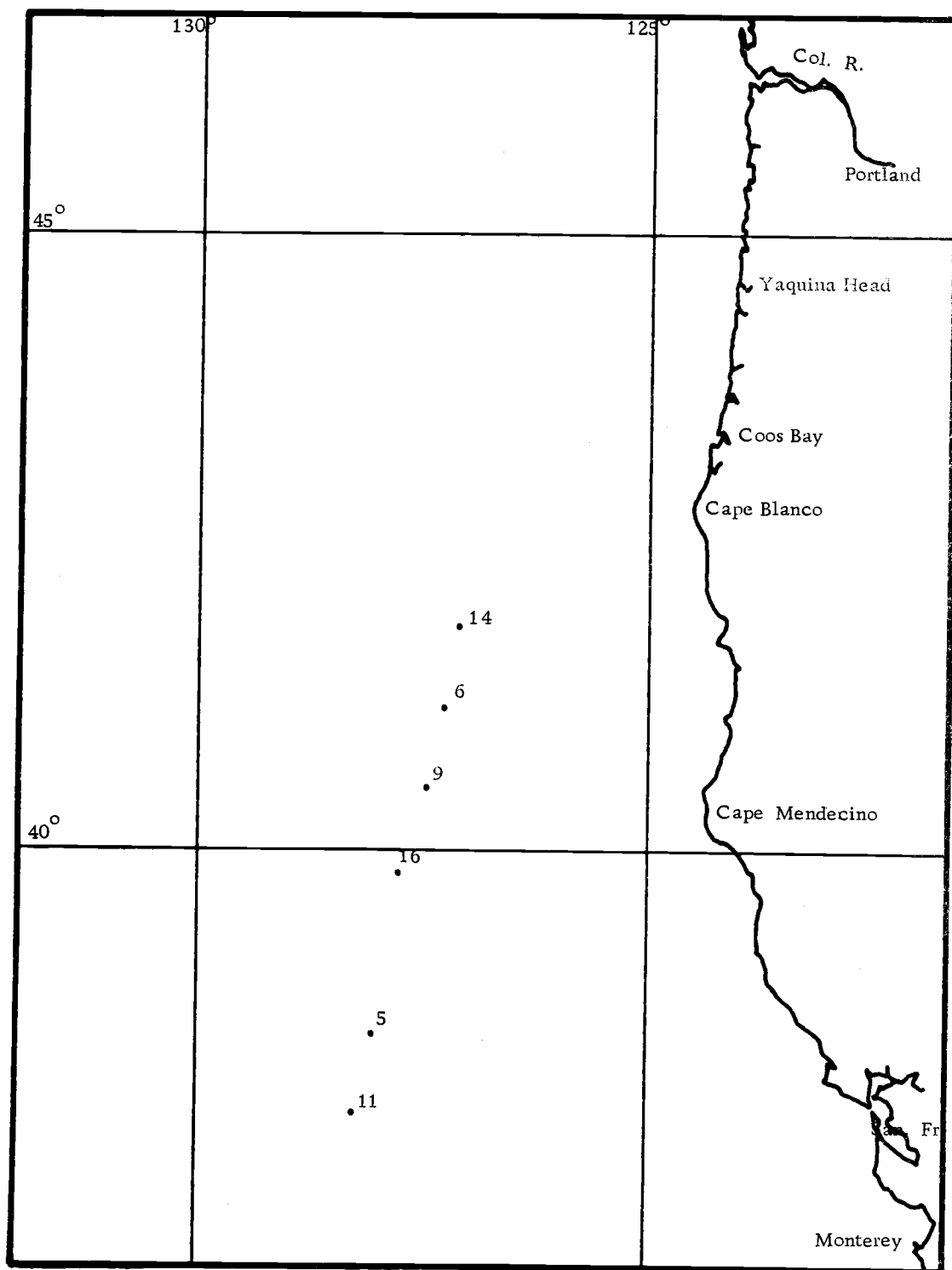


Figure 13. Values of zinc (ppb) at a depth of 100 meters from "WG" cruise, August 1966.

CONCLUSIONS

Extraction without filtration has proven quite good and reasonably free of contamination. The percent recovery is calculated to be about $97 \pm 5.4\%$ (standard deviation), with contamination ranging from zero to 0.8 ppb in the original sample.

With filtration, additional contamination occurs (about 0.5 to 2.4 ppb in the original sample), giving an overall median contamination of 1.4 ± 1 ppb for sea water analysis.

DISCUSSION

The need for filtration varies with the sea water sample. For surface samples with a high organic and particulate content, filtering is desirable. However, surface samples also tend to be higher in zinc content than deep water samples, and the contamination resulting from filtration is relatively less. Since deep samples are low in particulate matter, there is little to be gained (except for consistency) in exposing these samples, normally low in zinc content, to the possible contamination from filtering.

Regardless of whether the samples are to be filtered or not, the need for immediate analysis exists, and the lag between sampling and analysis should be kept to a minimum.

Some suggestions for future work along this line are:

1. Use another base or purify the ammonia used in the filtration process to eliminate this known and controllable contaminant.
2. Devise a new sampling method for deep samples.
3. Experiment with methods for storage of sea water samples so that analysis could be postponed. Investigation of acid addition and storage in polyethylene should be made.
4. Make use of the potential for a larger concentration factor by varying the amounts of MIBK and HCl and by varying the volume of the resulting product. Be sure to control the contamination,

however, or this, too, will be concentrated proportionately.

5. Investigate further the possibility of spiking the sea water first with stable zinc, then filtering and running the sample. This was done once, hesitantly, as the fate of the spike relative to the particulate matter was unknown. The results of this trial were unsatisfactory.
6. Ash the filters from filtered samples and compare the zinc content with that of the water sample or with other ashed samples.
7. Examine further the effects of pH range upon the extraction efficiency.

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