① 전원　　　　④ Potentiometer
② Gauss Meter　⑤ μVmeter
③ 전자석　　　　⑥ Flowmeter tube

flowmeter pipe의 크기는 어쩔 수 없더라도 자석의 크기 축소에 의한 자장의 감소는 자속누실을 작게하는 자석 design을 함으로써 어느 정도 보상할 수 있다.

본 실험에서는 유속이 큰 경우에는 별 문제가 안 되므로 유속이 0.5 m/sec≈1 knot 근방에서, 특히 본 실험에 사용된 계기로 측정이 가능한 한도내에서 작은 자장, 작은 유속에 의한 기전력을 관심에 두고 관찰하였다. 그림 4와 5의 data에 의하면 200gauss 자장에서 유속 0.1 m/sec≈0.2 knot 정도까지 0.5 m/sec의 유속에 대해서는 50 gauss 정도의 자장으로써도 기전력 측정이 가능했다.

따라서 자속누실을 작게 design한 소형자석과 내부저항이 충분히 크고 측정 Range가 좀 더 작은 측정계기 set를 사용할 경우 flowmeter가 상당한 규모로 소형화 될 수 있고 경제성까지 고려해서 국산실용화가 가능함을 결론으로 얻을 수 있다.

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Determination of Copper, Lead, Cadmium and Zinc in Water by the Square Wave Polarography with Dithizone-Chloroform Extraction Method

By

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Su-Chan Moon

디디존ー크로로포름 抽出, 矩形波 포ー라로그라피에 依한 水中의 구리, 납, 카드뮴 및 亞鉛의 定量

朴　相　潤

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Abstract

A combination of square wave polarography with the dithizone-chloroform extraction method was applied to the simultaneous determination of trace amounts of copper, lead, cadmium and zinc in water. When those ions forming dithizone chelate in chloroform layer were back-extracted with aqueous solution of 0.5 N KCl-0.1N HCl containing an excess of mercuric ion, the only free metal ions were extracted into aqueous layer. This aqueous solution was washed with chloroform twicely and polarograms were recorded directly without further treatment. This method can be used to determine the concentrations of copper, lead and cadmium up to about 3 ppb and of zinc 14 ppb with an error of 10%.

要　約

水中에 極微量 存在하는 구리, 납, 카드뮴 및 亞鉛을 디디존ー크로로포름 溶液으로 抽出한 것

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올, 디디존에 對하여 약간 過量의　水銀(Ⅱ)이온을 含有한 0.5 N KCl－0.1 N HCl 水溶液으로
逆抽出하여 크로로포름으로 두번 씻은 다음 바로 矩形波 포—라로그램을 그려서 3 ppb 以上의
구리, 납 및 카드뮴과 14 ppb 以上의 亞鉛을 10% 以內의 誤差로 同時 定量할 수 있었다.

1. Introduction

Recently, water pollution is becoming a serious problem and many investigations have been made
in regard to the determination of trace amounts of contaminated metal ions in water. In order to
detemine the ppb order of copper, lead, cadmium and zinc in Water, various combinated method
have been investigated. Solvent extraction method combined with colorimetry[1,2], electrochemical[3]
and atomic absorption method[4], X-ray spectrometry with absorption on ion exchange membrane[5],
and square wave polarography with anodic stripping polarography[6], ect.

Solvent extraction has been long used as a valuable tool for the separation and concentration of
minute constituents a sample, and it is a excellent pretreatment for the analysis of traces.

In order to apply an electrochemical method, such as polarography, to the analysis of the
extracted material in organic solvent, the sample solution had either to be evaporated or re-
extracted alternatively by an aqueous phase and treated appropriately prior to the application[6,7],
Use of a ternary mixture as a solvent in polarographic analysis[1,3], can be avoided the evapo-
ration or the re-extraction, but this method is thought to be not effective for the concentration of
minute constituents.

In this investigation, the dithizone-chloroform extraction method was combined with the square
wave polarography for the analysis of ppb order of copper, lead, cadmium and zinc in water.
when the dithizone-metal chelate in chloroform layer is back-extracted with aqueous solution cont
aining an excess of mercuric ion, the only free metal ions come into aqueous layer and the dithizone
remaines in chloroform layer foming stable chelate with mercuric ion. The excess of mercuric ion
and a small amount of dissolved chloroform in aqueous solution do not interfere with the square
wave polarographic determination of those metal ions.

2. Experimental

(1) Reagents

All the chemicals used were analytical reagent grade, and chloroform, ammonium water and
hydrochloric acid were redistilled before use.

0.01 M solutions of metal ions were prepared from suitable salts or metals and standardized by
EDTA titration. These solutions were stored in polyethylene bottles and diluted before use.

A 0.02% dithizone solution of chloroform was prepared by means of a conventional method[1].

Solutions of potassium chloride, 1 N ammonium citrate and a 20% hydroxylaminehydrochloride
and distilled water used for the preparation of calibration curves, were extracted with the

dithizone-chloroform solution before use.

(2) Apparatus

A square wave polarograph, Yanagimoto PA-202 (Japan), was used, and the characteristics of the dropping mercury electrode and recording conditions are as follows: H = 65 cm, t = 4. 00 sec., m = 1. 146 mg/sec., S. W. volt = 20mV, Gate Ⅰ = 2 − 7, Gate Ⅱ = 3 − 8, Time const = 5. 5, Pararell Capacitance = 100 μF, Recorder Sens = 0. 1 μA/mm, Ampf. Sens = 1/5 − 1/10, Volt. Sweeping = 2V/ 10 min., and polarograms were recorded from 0. 0 V to-1. 2 V vs. Hg-pool at 25±1℃.

(3) Extraction of metal ions

Metal ions were extracted with dithizone-chloroform by a conventional method[1], but the sample solutions were adjusted at pH 9. 5 − 10. 0 for prevention of tin (Ⅱ) ion extraction.

3, Results and Discussion

(1) Back-extraction with aqueous solution

From the fact that mercury (Ⅱ)-dithizone chelate is more stable than those of copper, lead, cadmium and zinc in carbon tetrachloride[11], it is thought that when these metal ions forming chelate with dithizone in chloroform are re-extracted with aqueous solution containing an excess of mercuric ion, they can be easily back-extracted into aqueous layer. In order to examine back-extraction and the dependance of pH on the rate of back-extraction 10 ml of the 0. 02% dithizone-chloroform solution containing 10⁻⁵M metal ions were extracted with 10 ml of aqueous solution of various pH containing 10⁻¹ M mercuric ion. In this case, zinc, cadmium and lead ions were extracted into aqueous layer quantitatively within 3 minutes, and the rate of extraction was independant of the pH in the range of pH 1 − 8. The back-extraction rate of copper ion, however, decreased as the pH increased as shown in Fig. 1.
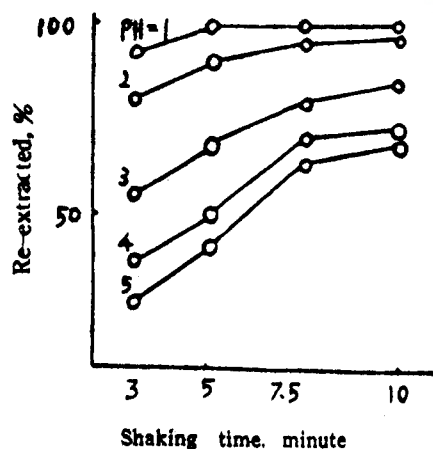

Fig. 1. Dependance of pH on the back-extraction rate of Cu with aqueous solution of 0. 5N KCl-10⁻¹M HgCl₂. Buffer solution: HCl+CH₃COOH

(2) Selection of supporting electrolyte

Potassium halides, thiocyanate and nitrate, hydrochloric acid and ammonium chloride are useful as supporting electrolyte in the square wave polarographic determination of these metal ions[11].

Potassium bromide, iodide and thiocyanate, however, are disadvantageous because of the formation of complex ion with mercuric ion and interfering with the backextraction. The peak of zinc ion in A. C. polarography is insensitive in the nitrate solution.

A small amount of mercuric ion in the solution does not interfere with determination of metal ions in A. C. polarography, but when the concentration of mercuric ion is greater then 10^{-3}M, a polarographic maximum of mercuric ion appears and interfere with the determination of the metal ions. This interference increases as the concentration of acid increases and that of salt as supporting electrolyte deceases. By the use of proper surface active substances, such as gelatine and polyacrylamide, this inteference can be eliminated [10], But these maximum supressor affected the wave height of lead, cadmium and zinc. Therefore, any maximum supressor was not used in this method.

Fig. 2. Dependance of gelatine on the wave heights. S. E. :0.5N KCl+0.1N HCl+4×10⁻⁴M HgCl₂. Metal ions:8×10⁻⁴M

Fig. 2 shows the dependance of the gelatine on the wave height.

An acidic solution is necessary for the rate of back-extraction. However, as the concentration of the acid increases, it produces the undesirable hydrogen peak which interfere with the determination of a small amount of zinc, and the interference of mercuric ion increases too.

Taking account of these conditions, the mixture of 0. 5 N potassium chloride, 0. 1 N hydrochloric acid and 4 x 10⁻⁴ M mercuric chloride was used in the back-extraction and as supporting electrolyte. The dependance of the concentration of hydrochloric acid and that of the concentration of potassium chloride on the wave height of these metal ions are shown in and Fig. 3 and in Fig. 4. Fig. 5 shows the calibration curves prepared from the standard solutions of metal ions in this supporting electrolyte by on may of the extraction and back-extraction. The peak potential of copper, lead, cadmium and zinc are determined to be −0. 27V, −0. 46V, −0. 66V and −1. 03V, vs. Hg-pool respectively. The calibration curves for copper
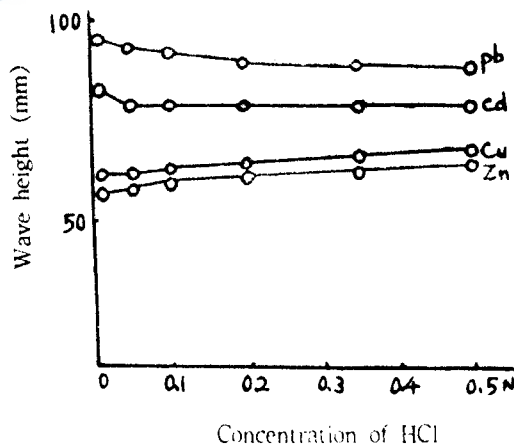

Fig. 3. Dependance of the concentration of HCl on the wave heights. Zn:3.2 ×10⁻⁴M Other Metal ions: 8×10⁻⁴M S. E. :0.5N Cl⁻(KCl) + 4×10⁻⁴M HgCl₂

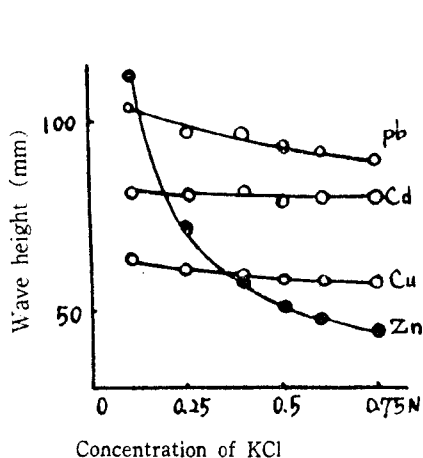and zinc were fairly linear but those for lead and cadmium were curved slightly.

Fig. 4. Dependance of the concentration
of KCl on the wave heights.
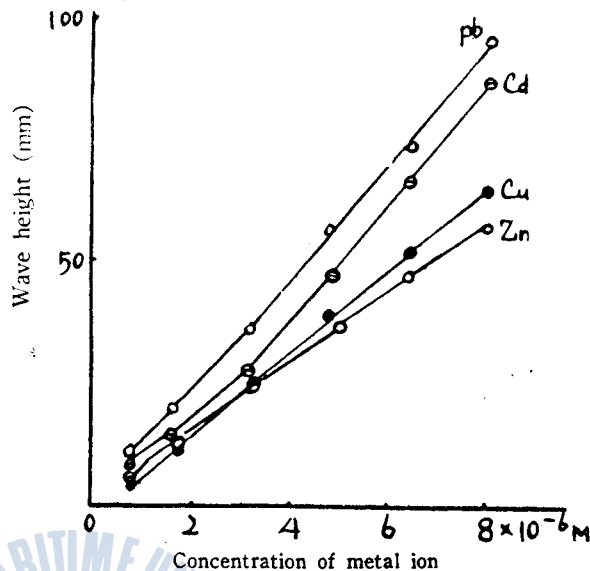S. E. : 0. 1N HCl+4×10⁻⁴M HgCl₂
Metal ions : 8×10⁻⁶M

Fig. 5. Calibration curves of metal ion from the
original standard solution. S. E. : 0. 5N KCl-0. lN
HCl-4×10⁻⁴M HgCl₂ Zn: 2. 5×10⁻⁶M

(3) Washing of the back-extracted aqueous solution

When the back-extracted aqueous solution from the chloroform layer was directly recorded polarograms, the polarographic waves of copper and lead were anomalous, compared with those of copper and lead recorded from the original solutions. This anomalous behavior is now under investigation, and is thought to be ascribed to the presence of a trace amount of suspending mercury-dithizone complex. This anomalous phenomenon, however, could be eliminated by means of washing the aqueous solution with pure chloroform for two or three times. Fig. 6 shows the results of washing.

(4) Recovery test

In order to test the reliability of the new method, recovery test were carried out with standard solutions. The procedure is as follows. A 500 ml of sample water is taken into a
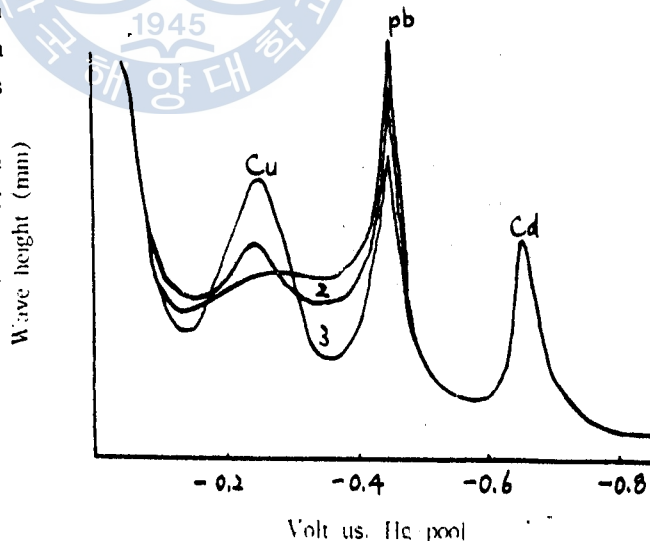

Eig. 6. Effect of washing with pure chloroform on the
polarograms of Cu⁺⁺, Pb⁺⁺ and Cd⁺⁺ after back-
extraction 1; not washed, 2; washed one time, 3;
washed two time. S. E. : 0. 5N KCl +0. 1 N HCl
containing 4×10⁻⁴M HgCl₂

fractional funnel, and 10 ml of 1 N ammonium citrate and 2 ml of the 20% hydroxylamine hydrochloride are added. After the pH is adjusted to pH 9.5－10.0 with 6 N ammonium hy droxide,   the solution is extracted with 10 ml of the   0.02% dithizone-chloroform repeatedly till chloroform layer remaines green.

The chloroform layer is collected and back-extracted with 10 ml of the aqueou solution of 0.5N +0.1N HCl+4x10^{-1} M HgCl$_2$. The aqueous layer is twicely washed with chloroform and the square wave polarograms are recorded in the voltage range 0 to－1.2V vs. the mercury pool at 25±1℃ after passing nitrogen gas for 10 minutes.

Table 1 shows the results determined five times with the standard solutions by this method. When the concentrations of copper, lead and cadmium are greater than 3 ppb and that of zinc 14 ppb, they can be determined with an error of approximately ±10%.

(5) Influence of foreign ions

In this method, the expected foreign ions for interference and their permissible amount are shown in Table 2.

Table 1. Results of determination

No	Cu taken ppb	Cu found ppb	max. error %
1	1.06	1.34±0.14	35.8
2	2.11	2.29±0.18	11.7
3	4.23	4.06±0.26	10.3
4	6.34	6.25±0.34	7.1
5	8.46	8.55±0.30	4.7
6	10.57	11.08±0.64	10.4

No	pb taken ppb	pb found ppb	max. error %
1	2.81	2.71±0.07	5.0
2	3.51	3.57±0.40	8.9
3	5.62	5.48±0.04	6.0
4	7.03	7.07±0.63	9.4
5	14.06	13.90±1.45	9.1
6	21.09	20.00±0.89	8.3

No	Cd taken ppb	Cd found ppb	max. error %
1	1.86	1.76±0.07	9.1
2	3.71	3.58±0.31	9.2
3	7.42	6.96±0.69	10.0

4	11. 14	10. 81±0. 34	5. 2
5	14. 85	14. 71±0. 22	2. 1
6	18. 56	18. 30±0. 32	3. 1

No.	Zn taken ppb	Zn found ppb	max. error %
1	3. 48	5. 33±0. 65	27. 0
2	6. 96	7. 50±0. 43	13. 9
3	13. 92	14. 92±0. 53	10. 9
4	20. 88	21. 20±1. 82	9. 5
5	27. 84	27. 15±1. 20	5. 8
6	34. 80	35. 20±1. 73	5. 3

Table 2. Influence of foreign ions.

Ions	Approximate limit of interference	
Bi (Ⅲ)	4 times of	Cu (Ⅱ)
Cu (Ⅱ)	50 〃	Pb (Ⅱ)
Pb (Ⅱ)	200 〃	Cd (Ⅱ)
Ni (Ⅱ)	2 〃	Zn (Ⅱ)
Co (Ⅱ)	20 〃	Zn (Ⅱ)

(6) Analytical application

Applications for the determination of copper, lead, cadmium and zinc in several kinds of water are shown in Table. 3.

Table 3. Applications for the analysis of metal inns in several kinds fo water.

Content (ppb)

| Ions / Sample	Cu	Pb	Cd	Zn
Running water	1. 5±0. 3	4. 8±0. 1		47. 0±0. 4
Distilled 〃	3. 6±0. 3	3. 7±0. 1		7. 0±0. 1
Re-distilled 〃	0. 6±0. 1	1. 4±0. 1		6. 4±0. 4

Running Water : taken at laboratory led from the gathering ground in Pusan University.

Distilled water : prepared by use of a distilliator, Samwha(Seoul), which was made of stainless steel and copper.

Redistilled water : prepared from the distilled water using hard-glass wares.

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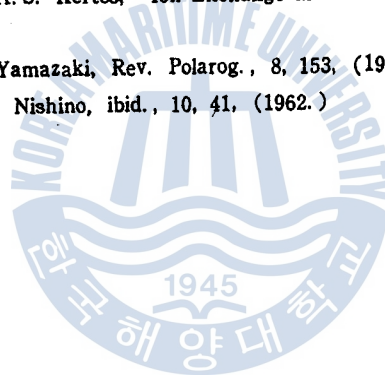
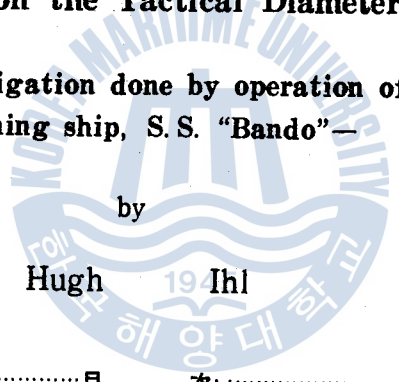# 船舶의 吃水와 速力의 變化가 旋回徑에 미치는 影響

——練習船 半島號簂 中心으로——

許 逸

Effects of the Alternation of Ship's Draft and Speed on the Tactical Diameter

—This investigation done by operation of the training ship, S.S. "Bando"—

by

Hugh Ihl

Abstract

Tactical diameters accordance with different loading and speed are measured repeatedly by operation of the training ship, S.S. "Bando", a medium-size cargo ship, and the alternation tendency of the tactical diameter is studied through generalization and analysis of experimental results.

1. 序 論

선박을 효율적으로 조선(操船)하기 위해서 조선자(操船者)가 알아야 할 가장 초보적이고 중