

I.O.S.

A method for determining cadmium, copper and  
nickel in marine sediment pore water samples

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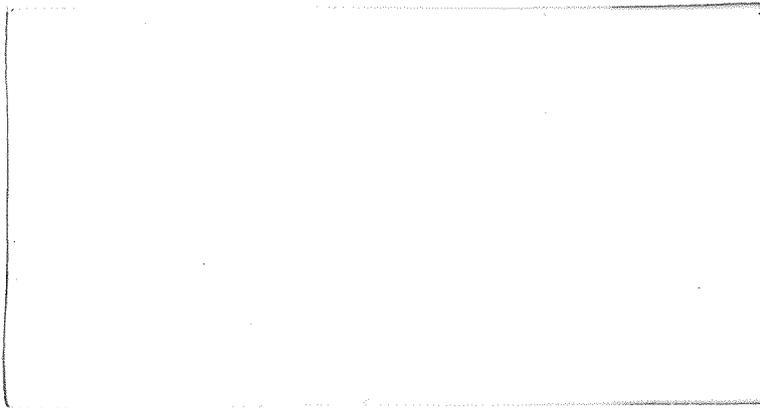
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## Introduction

We wish to study the distributions of dissolved trace metals in marine sediments both to understand the processes by which these metals are redistributed between different facies as a result of diagenetic reactions, and to use what we know of the chemistry of these metals to further our understanding of the active redox state in sediments. Anoxic conditions in sediments produce sufficiently elevated concentrations of iron and manganese in solution that their concentrations can be determined directly, by injection of pore water into a heated graphite furnace atomic absorption spectrophotometer (GFAA)<sup>1,2</sup>. However copper, nickel and cadmium are present at much lower concentrations (Cu <100nM; Ni <100nM; Cd <6nM) and so cannot be determined accurately by direct injection.

We chose to develop a method based on that of Danielsson<sup>3</sup>, which has recently been employed with some success in the Oceanography Department at Southampton University for the concentration of these elements from seawater<sup>4</sup>. The aim was to simultaneously extract all the metals of interest into a simple matrix for injection into the G.F.A.A.; and to produce a five-fold increase in concentration. In outline the method is:- formation of dithiocarbamate complexes of the metals, extraction into freon to separate them from the sea salt, and then back

extraction into nitric acid prior to injection into the G.F.A.A.

### Experimental

All of the following experiments were carried out in the I.O.S. clean room to reduce airborne contamination. To reduce contamination gloves and a nylon coat were worn throughout the experiments.

Determination of the metals was carried out using an Instrumenation Laboratories 655 graphite furnace atomiser coupled with an I.L.151 AA/AE spectrometer, using I.L. hollow cathode lamps as the light source.

Previous use of the atomiser for analyses of manganese and aluminium by directly injecting seawater had caused copper salts to be leached from the brass components of the furnace. During the high temperatures reached during atomisation some of this copper tended to transfer to the graphite cuvette contaminating it. To prevent this source of contamination the interior of the furnace is regularly cleaned using cotton buds and water.

### Reagents

Standard solutions of the metals were prepared from "Spectrosol" standard solutions. The buffer was a 0.5 molar solution of "AnalaR" di-ammonium hydrogen citrate, the nitric acid was "Aristar" grade. All of the above reagents

were supplied by B.D.H. Chemicals Ltd. Poole. The complexant was a 1% (w/v) solution of ammonium pyrrolidine dithiocarbamate (APDC) and diethyl ammonium diethyl dithiocarbamate (DDTC) (0.5g each + 100ml water) supplied by Hopkin and Williams Chadwell Heath.

The organic solvent was Colclene (1,1,2-trichloro-1,2,2-trifluoro-ethane Du Pont's Freon TF) supplied by Alexander Cole Ltd., London and will be referred to in the text as freon.

#### Preparation of reagents

The water used in these experiments was doubly distilled in a quartz still and then sub-boiling distilled and is referred to in the text as S.B.D. water.

The p.H.5 buffer is cleaned by carbamate extraction until 30 $\mu$ l of buffer in 0.5ml S.B.D. water gives a machine response below the detection limit (Note - direct injection of the buffer solution gives a poor machine response owing to the complex nature of its matrix).

The A.P.D.C./D.D.T.C. mixture is cleaned by shaking with successive portions of freon until 30 $\mu$ l in 0.5ml S.B.D. water gave a machine response below the detection limit. The cleaned solution is then stored over freon, so that any contamination developing during storage will be extracted into the freon.

The freon was cleaned by sub-boiling distillation.

Sea water, for use in blank determination, was prepared by placing 80ml of surface seawater in a separating funnel, adding 1ml of buffer solution, 1ml of complexant solution, 20ml of freon and shaking for ten minutes on a reciprocating shaker. After discarding the freon another 20ml of freon is added, shaken and discarded.

After addition of another 1ml of complexant and two washes with freon the sea water is effectively "stripped" of all the trace metals of interest.

Extraction of metals from the sea water to prepare blank by the above method appears to be much less efficient than the extraction efficiency achieved during the processing of samples. This may be due to more effective mixing of the small volumes used during sample processing.

#### Preparation of plastic ware

Test tubes and tops are cleaned by soaking in 6N nitric acid for three days, rinsing with doubly-distilled water, soaking again for three days in 6N hydrochloric acid, rinsing with doubly-distilled water and finally leaving to dry in a clean air laminar flow hood. The pipette tips were acid cleaned by soaking overnight in 6N hydrochloric acid.

## Procedure

Place seawater (2.5ml) in a clean test tube, adjust pH to 5 by adding buffer solution (30 $\mu$ l) using a Howe micropipette, add, simultaneously cleaned complexant (30 $\mu$ l) and freon (1ml) (add the freon from a dispenser (Oxford) as it has a low surface tension which makes pipetting difficult). Shake this mixture for 10 minutes and leave to settle for 2 minutes and remove the aqueous (upper) layer. Add S.B.D. water (1ml) shake gently for 2 minutes allow to settle for 2 minutes and discard the aqueous layer making sure that as much of the aqueous layer is removed as possible. Add nitric acid (30 $\mu$ l) shake for 5 minutes and allow to stand for 5 minutes, add S.B.D. water (0.5ml) shake for 2 minutes leave to settle for 2 minutes and pipette off the freon (lower layer). The sample is now ready for determination by G.F.A.A.

## Preliminary studies

This method was initially developed for nickel as it is the least likely to give contamination problems.

Danielsson's method recommends two extraction steps on the same sample, however if two extractions were performed it would involve transferring the aqueous layer to a new test tube which could increase the problems of contamination. When this extraction procedure was carried out without a washing step several results were lower than

expected (see Fig.1). These low results could be caused by (i) salt being carried over which would reduce the G.F.A.A. signal or (ii) buffer solution being carried over which would reduce the efficiency of the back extraction.

A little of the aqueous layer is likely to be carried over as it is almost impossible to completely remove the aqueous layer as the last drop forms a fine film over the surface of the freon. Repeated pipetting to remove this layer is not advisable as it would tend to (i) introduce contamination and (ii) increase the loss of freon.

A washing stage reduces the effect of salt or buffer carry over and so was introduced (compare Figures 1 and 3).

#### Graphite furnace operation

The final 5% nitric acid solution was stated by Danielsson to be well suited to G.F.A.A. and work by members of Southampton University, Oceanography Department has shown this to be the case, however in the I.L. system at I.O.S. it presented a major problem.

When a 10 $\mu$ l sample is injected into the furnace curvette and heated the droplet collapsed and "ran" down the curvette to a cooler area where it subsequently dried. (The curvette was not on a slope as the drop "ran" in both directions). This gave two problems (i) a very low signal and (ii) a build up of analyte in the curvette causing poor reproducibility (see Table 1). (In contrast a 5%

hydrochloric acid matrix dried perfectly and gave results of remarkable reproducibility (Figure 2).

With nitric acid it did not prove possible to use a "normal" drying program in which the curvette is heated slowly to dry the analyte drop smoothly.

The only way we found to prevent nitric acid "running" was to use "forcing" conditions - heating the curvette rapidly (see Table 3), causing the droplet to boil. Though boiling in the tube will reduce reproducibility (due to splattering) the advantage of the droplet staying in the centre region of the curvette outweighs this disadvantage (see Table 1).

When concentrated hydrochloric acid was used in place of nitric acid extraction efficiency was very low (Table 2) increasing the volume of acid used increased efficiency only slightly and introduced a large contamination problem from the acid. These findings are directly in contrast to statements in Danielsson's paper<sup>3</sup> and Statham's thesis<sup>4</sup> which suggested that any acid might be used to decompose the APDC/DDTC.

#### Blanks and contamination

For the determination of nickel consistently low reagent blanks were obtained when 2.5ml of aliquots of SBD water were passed through the extraction procedure. However when this was done as part of the copper determination the

blanks were high and the reproducibility poor. Tests showed the source of the contamination to be the test tube walls in which the extractions were being done. Placing 2.5ml of concentrated nitric acid in the tubes and shaking overnight prior to extraction of samples was found to reduce the copper blank, however this process elevated the nickel blank, possibly by action of the concentrated acid on the tube walls exposing nickel present in the plastic.

During the course of these experiments the S.B.D. water itself became contaminated to a level of 10nM copper. To avoid this problem it was decided to measure the blanks by passing freshly stripped surface seawater through the process.

A comparison of 4 cleaning methods (Table 4) was undertaken by cleaning five separate tubes by each method and determining the blank values for each element.

The results (Table 4) gave high blanks for all the cleaning processes, this is probably because in the preparation of the stripped seawater only two phase separations were carried out. However even with this problem it can be seen that cleaning the tubes with APDC/DDTC and freon gives the lowest and most most reproducible blanks.

The two tubes which showed the highest contamination were both acid cleaned tubes and indicated that copper and cadmium contamination may be linked.

A fresh determination of the reagent blanks was made using seawater stripped as described above in the preparation of reagents. Using the APDC/DDTC/freon method of cleaning the tubes, blank values of Cd-0.4nM, Cu-4nM and Ni-3nM were obtained. This compared to blank values of Cu-3nM and Ni-4nM reported by Sawlan and Murray<sup>2</sup> for their APDC co-precipitation procedure. Because "cleaned" reagents can become contaminated a check on the reagent blank should be made as a part of each set of extractions.

#### Reproducibility and efficiency

When four separate determinations were carried out on a sample of surface seawater spiked with 58.4nM of copper. The measured concentrations in the final nitric acid extracts were 273, 284, 288 and 305nM. Figures 3,4 and 5 show calibration lines for Cd, Cu, and Ni determinations. At each stage on the line two samples of spiked seawater were processed. Each final solution was then analysed 5 times on the G.F.A.A. and the individual peak heights are plotted on the graph. The precision of the determinations as indicated by these lines is Cd 0.25Nm, Cu 3nM and Ni 5nM. Comparison of the gradients of the lines in Figures 3, 4 and 5 with those obtained for standard solutions prepared directly in 5% nitric acid gives a measure of the efficiency of the extraction procedure. These are listed in Table 6, and are in line with earlier results for the application of

this extraction to estuarine waters<sup>5</sup>, although lower than Danielsson's<sup>1</sup> reported for his two stage freon extraction procedure.

### Summary

The method originally proposed by Danielsson<sup>1</sup>, has been successfully modified for use on small volume pore water samples. Because of the poorer ability to separate phases in the test tubes as compared to a separating funnel a washing step has been introduced to remove sea salt and buffer from the freon before back extraction into nitric acid. The nitric acid has to be removed from the freon phase before samples can be successfully pipetted into the G.F.A.A. this contrasts to Magnusson and Westerlunds<sup>5</sup> suggestion that this was not necessary. We confirm their observations<sup>5</sup> that nitric acid has to be used in preference to hydrochloric acid to decompose metal dithiocarbamate complexes.

Ten 2.5ml samples can be prepared for injection into the G.F.A.A. in one and a half hours.

#### REFERENCES

1. Hydes, D.J., *Anal. Chem.* 1980, 52, 959-963.
2. Sawlan, J.J. and Murray, J.W., *Earth. Planet Sci. Letts.*, 1983, 64, 213-230.
3. Danielsson, L.-G., Magnusson, B. and Westerlund, S., *Anal. Chim. Acta.* 1978, 98, 47-57.
4. Statham, P.J., Ph.D. Thesis University of Southampton, 1983, 209pp.
5. Magnusson, B. and Westerlund, S., *Anal. Chim. Acta.*, 1981, 131, 63-72.

Table 1

Effect of drying time on a 63nM 5% HNO<sub>3</sub> Sample of copper

Program 1: ambient to 220°C in 0 sec, 220°C to 220°C in twenty second then as Table 3.

Program 2: ambient to 90°C in 10 sec, 90°C to 140°C in 30 sec then as Table 3.

Program	Peak height of individual injections
1	32,33,30,34,30,34.
2	32,5,33,12,43,12,5,7,6.

Table 2

Use of concentrated hydrochloric acid for back extraction of copper carbamate complexes

Sea water spike	Mean peak height
0	0.5
23nM	0.75
23nM	0.75
38nM	1
59nM	1
59nM	1.5

Table 3

Graphite furnace atomiser conditions

Element Stage	Copper		Nickel		Cadmium	
	Time	Temp.	Time	Temp.	Time	Temp.
1	0 sec	220°C	0 sec	220°C	0 sec	220°C
2	20 "	220°C	20 "	220°C	15 "	220°C
3	15 "	800°C	15 "	600°C	15 "	350°C
4	5 "	910°C	5 "	610°C	5 "	350°C
5	0 "	2000°C	0 "	1900°C	0 "	1700°C
6	5 "	2000°C	5 "	1900°C	5 "	1700°C

Table 4

Test tube cleaning procedures

Procedure 1: Shake with 2ml APDC + DDTC and 2ml freon overnight.

Procedure 2: Shake with 2.5ml conc. HNO<sub>3</sub> overnight.

Procedure 3: Use tubes already used for previous extractions.

Procedure 4: Just the acid leach given to all the tubes.

All of the tubes were rinsed three times with SBD water prior to use.

Five tubes were cleaned by each procedure and the blanks determined for each element.

Cadmium

Procedure	Mean peak height of tubes	Mean concentration of 5 tubes	Standard Deviation
1	4.3,4.8,3.8,4.8,3.3	1.2nM	0.2nM
2	74, * 35, * 5.7,6,4.8	1.5nM	0.2nM
3	6.3,4.3,4.5,5	1.3nM	0.3nM
4	5,4.3,4.5,4.8,6.3	1.3nM	0.3nM

Copper

Procedure	Mean peak height of tubes	Mean concentration of 5 tubes	Standard Deviation
1	3.3,3,3.7,3.3,2.3	6nM	1nM
2	54, * 35, * 4.8,2.8,3.3	7nM	2nM
3	3.8,3.5,2.3,1.3	5nM	2nM
4	6.3,2.7,2.8,3.3,3	7nM	3nM

Nickel

Procedure	Mean peak height of tubes	Mean concentration of 5 tubes	Standard Deviation
1	2.7,3.3,3.0,4.0,4.2	14nM	2nM
2	9.5,8.5,8.5,7.5,10.5	36nM	3.5nM
3	5.3,4.5,3.8,4.0	17.5nM	2nM
4	4.7,3.5,4,3.3,4.7	16nM	2nM

\*These results not used to calculate the mean or standard deviation.

Table 5

Reagents blanks for the APDC/DDTC/freon tube cleaning procedure using stripped seawater prepared after four phase separations

Element	Mean peak height of tubes	Mean concentration of 5 tubes	Standard Deviation
Cd	1,0.7,1,3,0.7,1	0.4nM	0.1nM
Cu	2.4,2.2,1.5,1.9,1.8	4nM	0.8nM
Ni	1.1,0.6,0.7,0.5,1.1	3nM	0.5nM

Table 6

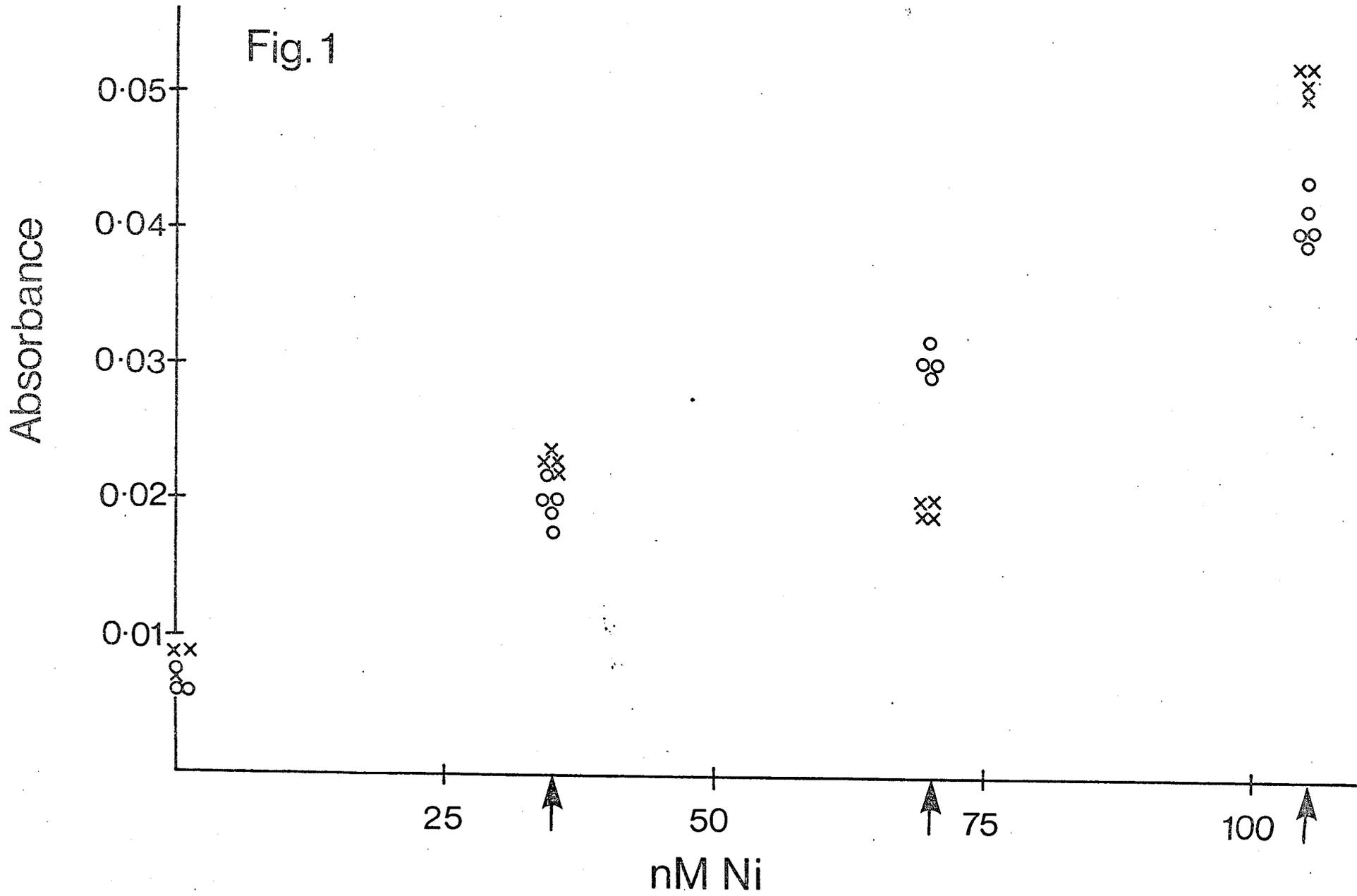
Efficiency of extraction

Element	Gradient of standards plot (absorbance nM <sup>-1</sup> )	Gradient of spiked samples plot (absorbance nM <sup>-1</sup> )	Efficiency %
Copper	$5.1 \times 10^{-3}$	$4.63 \times 10^{-3}$	99
Cadmium	$1.71 \times 10^{-2}$	$1.38 \times 10^{-2}$	86
Nickel	$5.00 \times 10^{-4}$	$4.12 \times 10^{-4}$	88

### Figure Captions

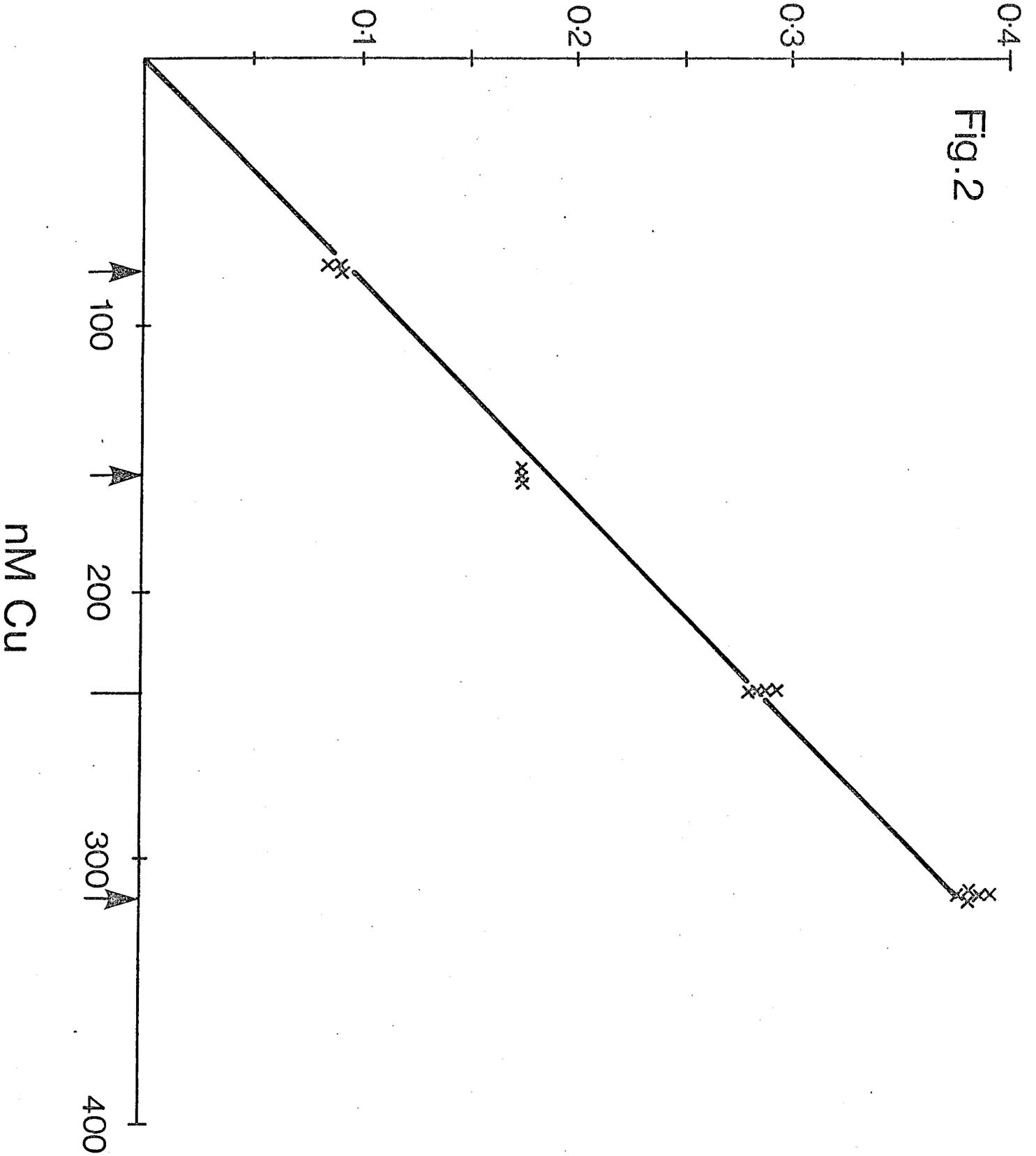
- (1) Calibration line for nickel spiked seawater determination carried out without washing step after removal of aqueous layer from freon extraction solution. Individual atomisations shown, x and o distinguish two samples at each stage.
- (2) Calibration line for standard solutions of copper in 5% hydrochloric acid.
- (3),(4),(5) Calibration lines for cadmium, copper and nickel spiked seawater respectively. Individual atomisation are shown, x and o distinguished two samples at each stage.

Fig. 1



Absorbance

Fig. 2



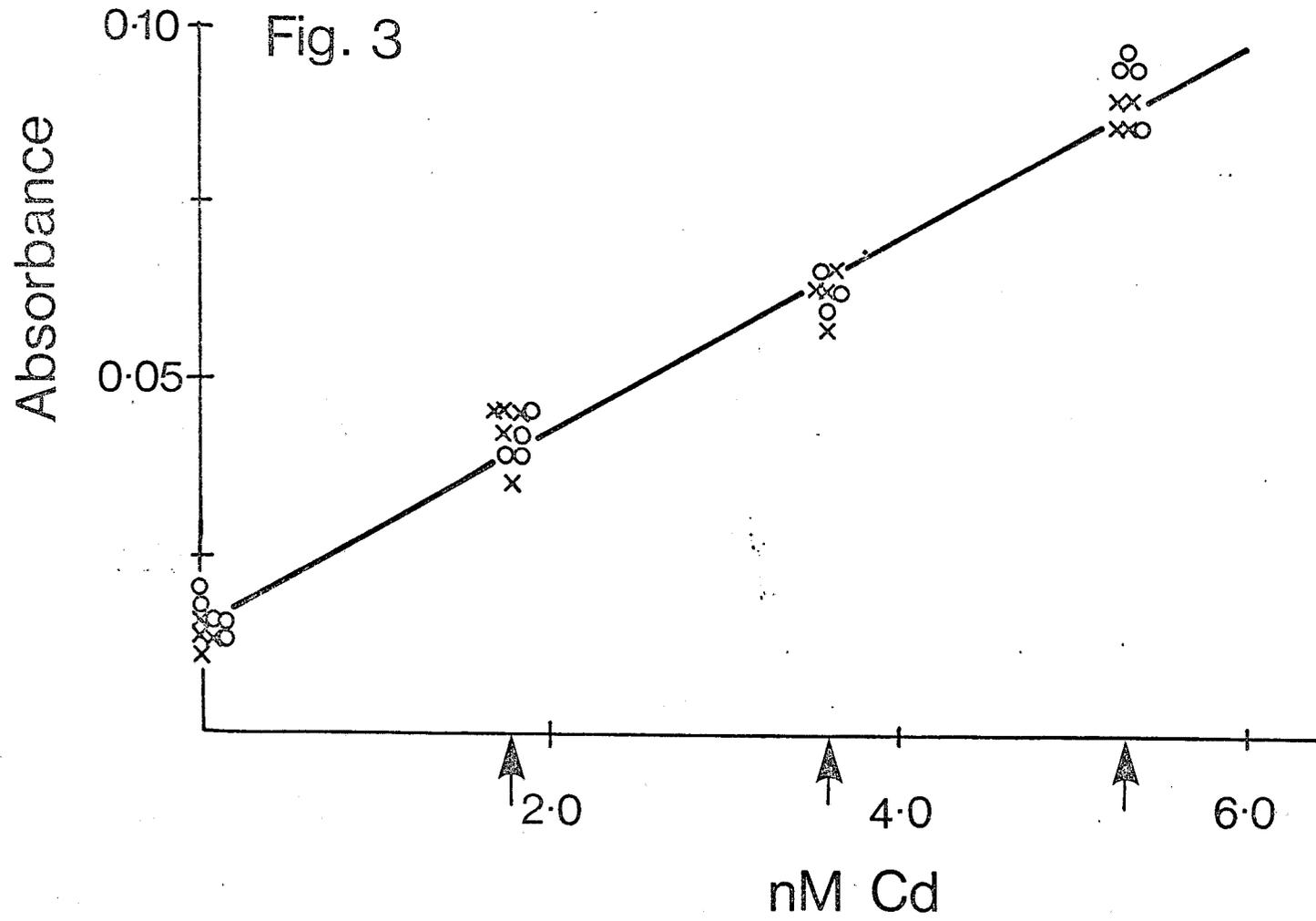


Fig. 4

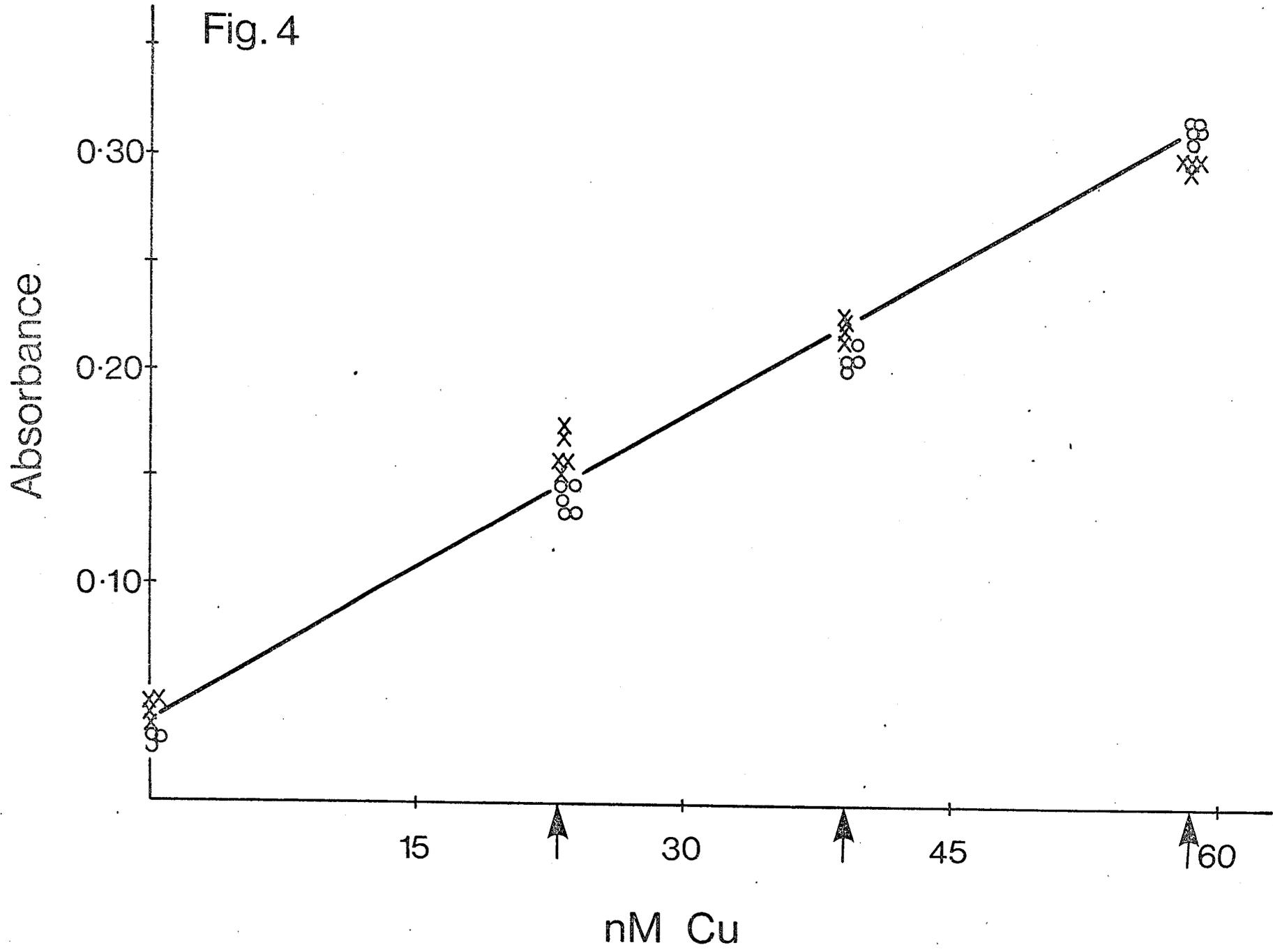


Fig. 5

