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A new method for the determination of trace metals in seston by flameless atomic absorption spectrometry

THÜNEN
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by

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The elementary composition of marine organisms has been studied by biologists and chemists since the last century[1,2]. These investigations however were chiefly subjected to the main components of sea-water. But due to pollution aspects studies on the accumulation of trace elements, especially heavy metals, got a high priority. Thus estimations of concentration factors in particulate organic matter as first link in the foodchain is of a special interest[3-6].

To analyse trace metals in particulate matter seston is ordinarily collected on filters and oxidised mainly in a wet digestion procedure with HCl, HNO_3 and H_2O_2[4,5,7]. A compilation of recommended methods is published by E.P.A.[8].

Lacking from the fact that filters used up to now have high blank metal values, much material has to be enriched requiring long filtration times. Furthermore manipulation with the reagents makes it difficult to avoid contamination effects during time consuming digestion processes.

Due to improvement of flameless atomic absorption spectrometry[9,10] and due to development of filter material with very low metal contents it was decided to make some further investigations on trace metal analyses in particulate matter.

This paper describes a method for the determination of selected metals in seston based on direct atomization and internal calibration in a heated graphite atomizer.

EXPERIMENTAL

Instrumentation

A Perkin-Elmer Model 403 atomic absorption spectrometer equipped with a Rikadenki Kokyo Model Mark II recorder, a deuterium arc background corrector and a Perkin-Elmer HGA-72 heated graphite atomizer was employed. This instrumentation has been described in detail by Welz[11]. Modification for copper analysis is described by Kremling and Petersen[12].

Nuclepore filters (General Electric Company) are used for collecting the seston from sea-water samples because of well defined pore size and their very low metal content (see Fig. 1 and Table 1). Reported analyses are in good accordance with the data found in this work.

Another advantage of the filters is their good solubility in chloroform, which can be easily purified (see Fig. 1) so that an overall low blank value is attainable.

Dissolving of the filters is performed in 50 cm^3-Erlenmeyer quartz flasks.

All additions of the reagents and sample injections are made by Eppendorf pipettes.

The plastic tips and the quartz flasks are cleaned in a MIBK/APCD solution as described eselwhere[12].

Reagents

Chloroform. Redistil the commercial grade reagent (Merck) very slowly in a quartz still; no blank value for the metals investigated here should then be detected (see Fig. 1).

Standard metal solutions. Prepare a standard stock solution (pH 2) of 1000 ppm Fe, Cd, Cu, Zn and Pb (Titrisol, Merck). From this stock solution prepare daily a 0.01 ppm working standard for Cu, Fe and Pb and a 0.001 ppm working standard for Cd and Zn by dilution.

Procedure

Seston is collected by filtering 500 cm^3 of sea-water through 47 mm Nuclepore filters (pore size 0.4 μm) and dried for 12 h at 70° C. Transfer the filter into a 50 cm^3 Erlenmeyer quartz flask and add 10 cm^3 chloroform by a calibration pipette. The filter is easily dissolved (in less than one minute), whereas the particulate matter is highly dispersed in the chloroform solution after putting the solution in an ultra sound bath for about 30 sec.. Shake fairly before starting the measurement by the atomic absorption spectrometer with the temperature programme as described in Table 2. For the injection of the chloroform phase take 10 to 50 μl pipettes depending on the concentration factors of the metals under investigation. The data reported in Table 3 were obtained by using 50 μl for Cu, Cd and Pb and 10 μl for Fe respectively. After evaporation of the chloroform step (1)[a] internal calibration is performed by direct injection of the working standard (20-75 μl) into the furnace.

The temperature programmes for the metals vary at the heat combustion step (2) due to the different atomization behavior. For all metals the atomization step (3) was carried out by GAS STOP programm providing an increased sensivity. With the exception of iron analysis, which requires a high atomization temperature, the grooved furnace is used.

A typical set of registration curves is given in Fig. 1 and 2. Fig. 1 demonstrates the qualification of chloroform and nuclepore filters as material for trace metal analysis. Fig. 2 shows the sensitivity of the procedure. The recorder speed was normally 2 cm min^{-1}.

CALCULATION OF RESULTS

The method for the calculation of the metal contents from internal calibration has been described elsewhere[12]. For fitting of the regression lines the method of least squares is applied. The precision of the whole procedure performed with a surface sample of Kiel Bight is given in Table 4. The standard deviation between 7 and 15 % is in the range of the wet digestion methods. Kremling (unpublished results) compared heavy metal analyses in order to digest the particulate matter using the method of the traditional wet digestion and the method described here. The results of both methods did not show any differences.

Some results determined with the procedure are shown in Table 3. The samples were collected from the Baltic Sea during the cruise with R.V. 'Alkor' in May 1973.

The weight of the particulate matter was in the range of 0.5 mg dm^{-3}. The particle size of the samples varied between 0.5 and 300 µm.

Details will be published elsewhere.

I would like to acknowledge Dr. Kremling and Mr. Petersen for helpful discussion.

SUMMARY

A quick and simple method is described for the determination of selected metals in seston by flameless atomic absorption spectrometry. Nuclepore filters are used for very low metal content. Digestion of the sample and internal calibration are directly performed in the HGA-72 graphite furnace. Replicate determinations of seston with a mean concentration of 18 ppm Cu, 1390 ppmFe, 43 ppm Pb and 6.8 ppm Cd showed standard deviation between 7 and 15 %.

ZUSAMMENFASSUNG

Eine schnelle und einfache Methode zur Bestimmung verschiedener Spurenmetalle im Seston mit Hilfe der flammenlosen Atom-Absorptions-Spektrometrie wird beschrieben. Wegen ihres niedrigen Metallgehaltes werden Nuclepore Filter verwendet. Der Aufschluß der Proben und die interne Eichung erfolgen direkt in dem Graphitrohr HGA-72. Die Reproduzierbarkeit liegt bei einer Konzentration von 18 ppm Cu, 1390 ppm Fe, 43 ppm Pb und 6.8 ppmCd zwischen 7 und 15 %.

RÉSUMÉ

On a décrit une methode opérant vitement et ayant simple, pour déterminer différentes trace éléments contenus en Seston par absorption spectrophotometrie atomique sans flammes. En considération de son contenue métallique bas, Nuclepore filtres sont utilisées. La digestibilité des matériaux des tests et le calibrage interne sont effectués directement dans la graphite tube cuvette HGA-72. En reproduire cette méthode concernant Seston avec 18 ppm Cu, 1390 ppm Fe, 43 ppm Pb et 6.8 ppm Cd, on a observé standard déviations entrè 7 et 15 %.

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Legends to the Figures:

Fig. 1:

Registration curves from 50 µl injections of chloroform (a), chloroform solution of 5 different filters (b), and replicate determinations of a seston sample (c).

Fig. 2:

A set of atomization peaks (with deuterium arc corrector) from internal calibration. "S" is indicated for sample probe.

Table 1:

Mean contents (µg per filter) of applied Nuclepore filters (40 CPR 04700)

Metal	This work	General Electric
Cu	0.04	0.05
Pb	0.00	----
Fe	0.03	0.5
Cd	0.00	----

Table 2:

Program for the HGA-72

Zn (213.9 nm)

Step	(1)[a]	(1)[b]	(2)[c]	(3)[d]	(4)[e]
Temp (°C)	65	100	600	1830	----
Time (sec)	60	60	60	10	60
GASSTOP	yes				

Cu (324.7 nm)

Step	(1)[a]	(1)[b]	(2)[c]	(3)[d]	(4)[e]
Temp (°C)	65	100	800	2200	----
Time (sec)	60	60	60	10	60
GASSTOP	yes				

Pb (283,3 nm)

Step	(1)[a]	(1)[b]	(2)[c]	(3)[d]	(4)[e]
Temp (°C)	65	100	520	2045	----
Time (sec)	60	60	60	10	60
GASSTOP	no				

Cd (228,8 nm)

Step	(1)[a]	(1)[b]	(2)[c]	(3)[d]	(4)[e]
Temp (°C)	65	100	275	1830	----
Time (sec)	60	60	120	10	60
GASSTOP	no				

Fe (248,3 nm)

Step	(1)[a]	(1)[b]	(2)[c]	(3)[d]	(4)[e]
Temp (°C)	65	100	1135	2540	----
Time (sec)	60	60	60	10	60
GASSTOP	yes				

a: Evaporation of chloroform b: Evaporation of standard solution

c: Heat combustion of organic material d: Atomization

e: Cooling period

Table 3:

Results of heavy metal investigations of Baltic seston

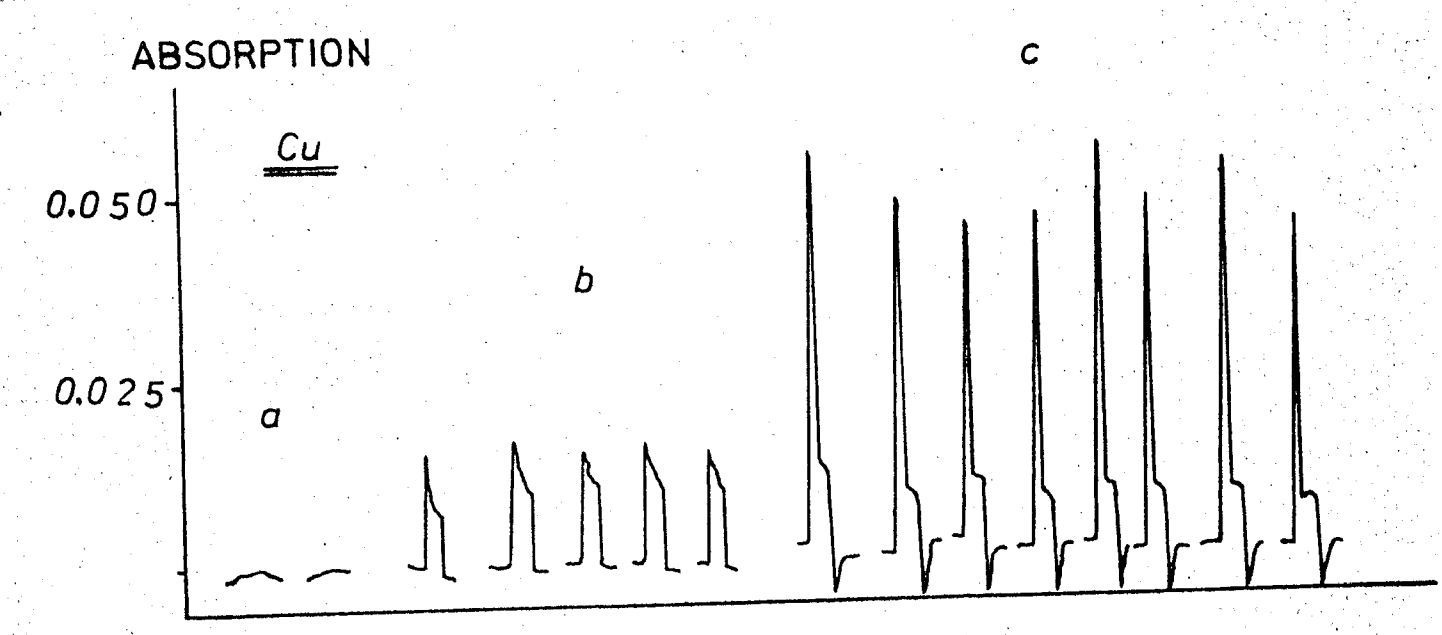
Metal	N	Mean concentr. (ppm)	Rel.Stand dev.(%)	Extrema
Pb	99	123	± 102	0-527
Cu	100	61	± 110	0-354
Cd	99	5,8	± 92	0-28,1
Fe	60	4475	± 123	514-17734
Zn	93	733	± 139	28-4758

(N : numbers of samples)

Table 4:

Coefficient of variation for replicate analyses

Metal	Rel.Stand. dev.(%)	Number of anal.	Mean concentr. (ppm)
Cu	11	7	18.0
Cd	7	8	6.8
Pb	9	8	43.0
Fe	12	7	1390.0
Zn	15	8	345.0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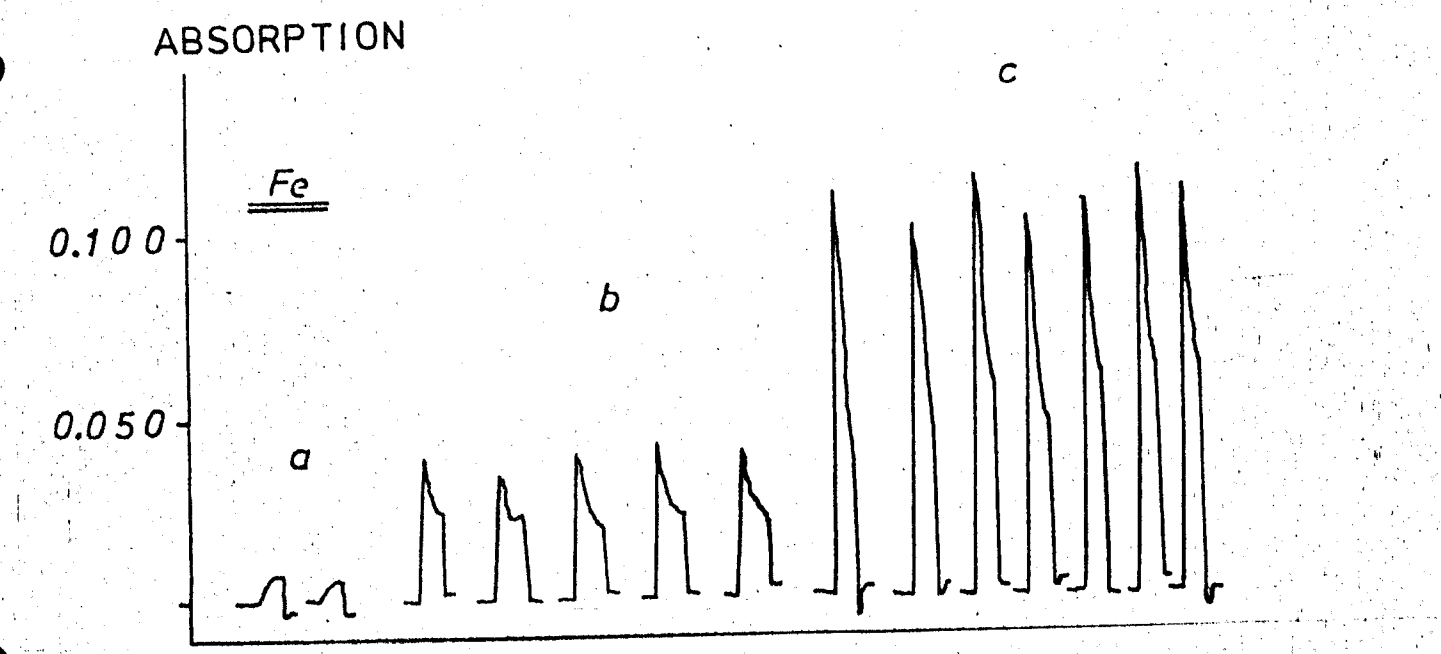
0.025
a
b
c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Fe
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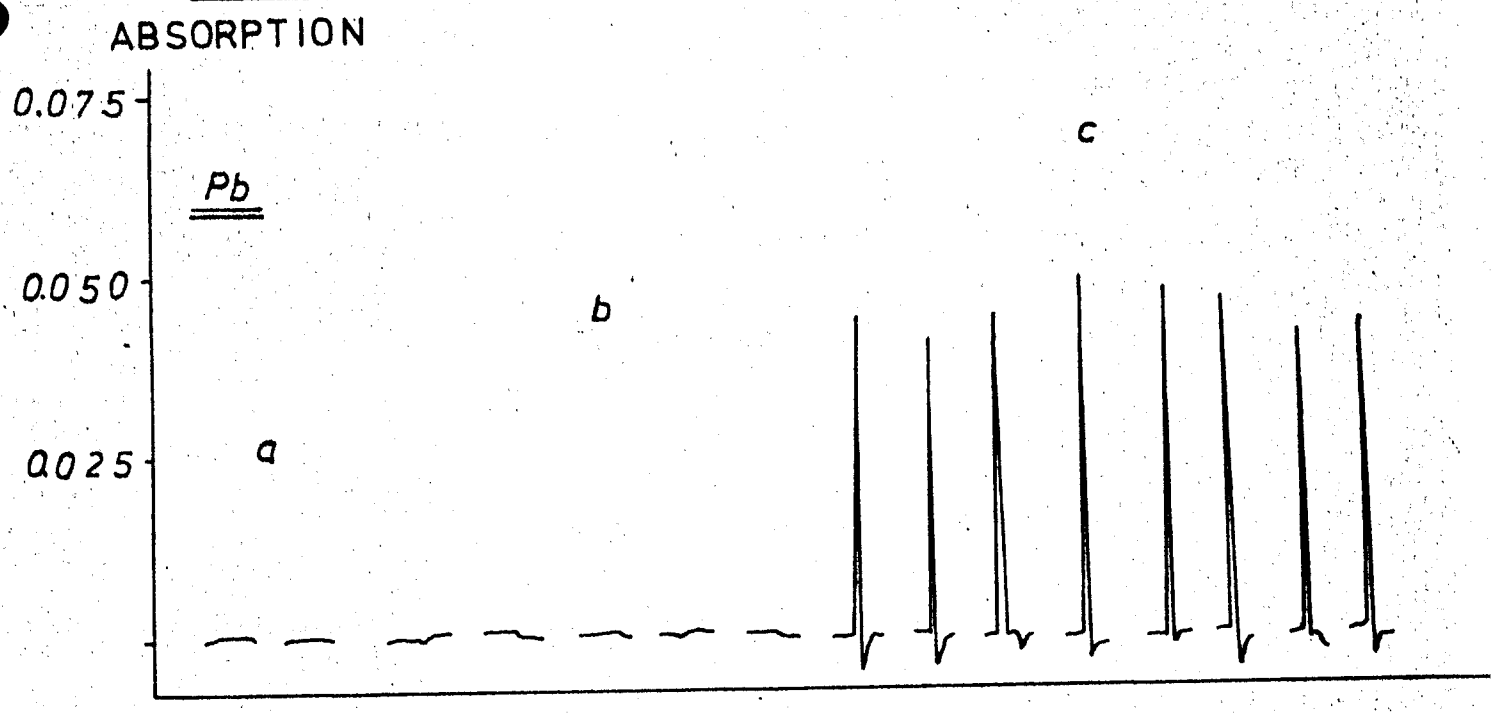
a
b
c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0.025
a
b
c

Fig. 1

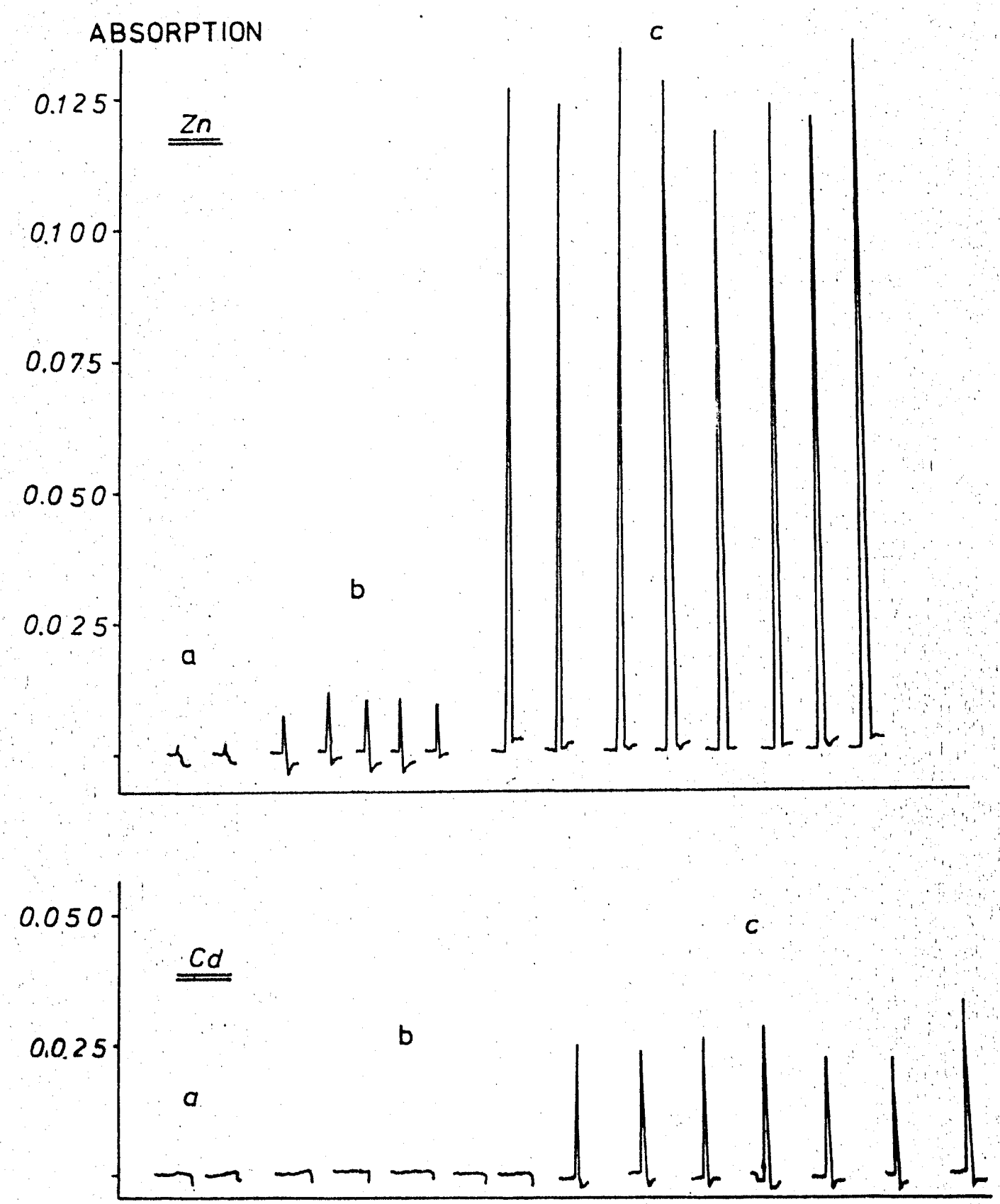
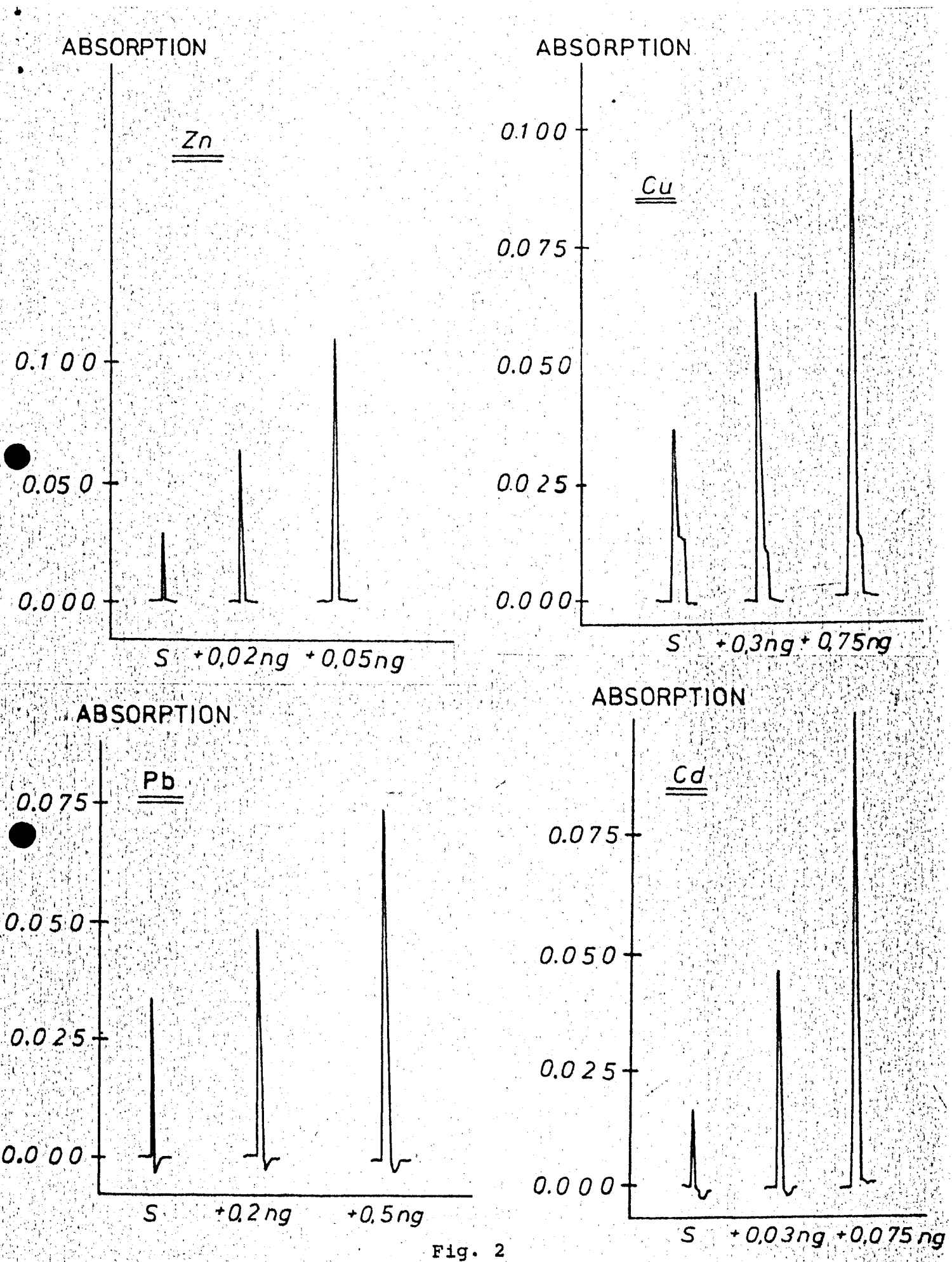


Fig. 1


ABSORPTION
Zn
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0.050
0.000
S +0,02ng +0,05ng
ABSORPTION
Cu
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0.050
0.025
0.000
S +0,3ng +0,75ng
ABSORPTION
Pb
0.075
0.050
0.025
0.000
S +0,2ng +0,5ng
ABSORPTION
Cd
0.075
0.050
0.025
0.000
S +0,03ng +0,075ng

Fig. 2

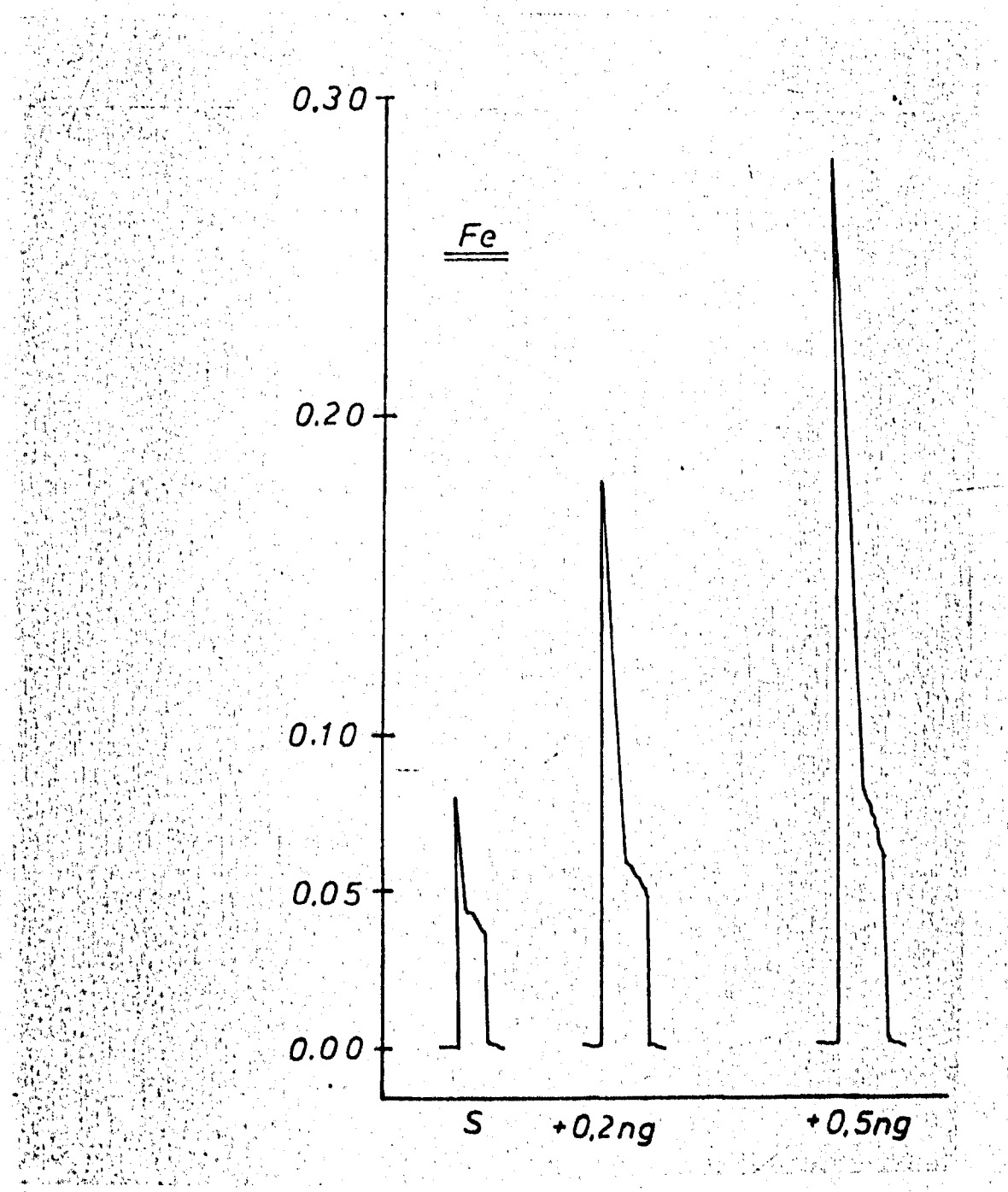

Fig. 2