

TECHNICAL REPORT

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Sorption by some North Sea Sediments

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The sorption properties of about seventy soil samples of the thousand points system were investigated up to now by means of four radioisotopes, namely : Cs¹³⁷, (Cs¹³⁴), Co⁶⁰, Mn⁵⁴ and Cd¹⁰⁹. Similar tests with Zn⁶⁵ are now being conducted actively. The methods and measuring systems used have been described in previous reports. Special attention was devoted to non-sandy samples which explains why most of the samples investigated derive from the South of the survey network and toward the coast. Figure 1 shows the specimens examined and their place within the thousand points system. About thirty new samples are being investigated in order to obtain a better spread over the entire area under survey. To note that further toward the Sea, the samples become increasingly sandy and the values for capacities and coefficients of distribution decrease significantly. As already premised in previous reports, the sediments rich in clay and silt are actually the only ones featuring high values for sorption. However, the contribution of sandy samples to sorption may not be neglected considering that these soils cover much larger surfaces.

North and bottom samples

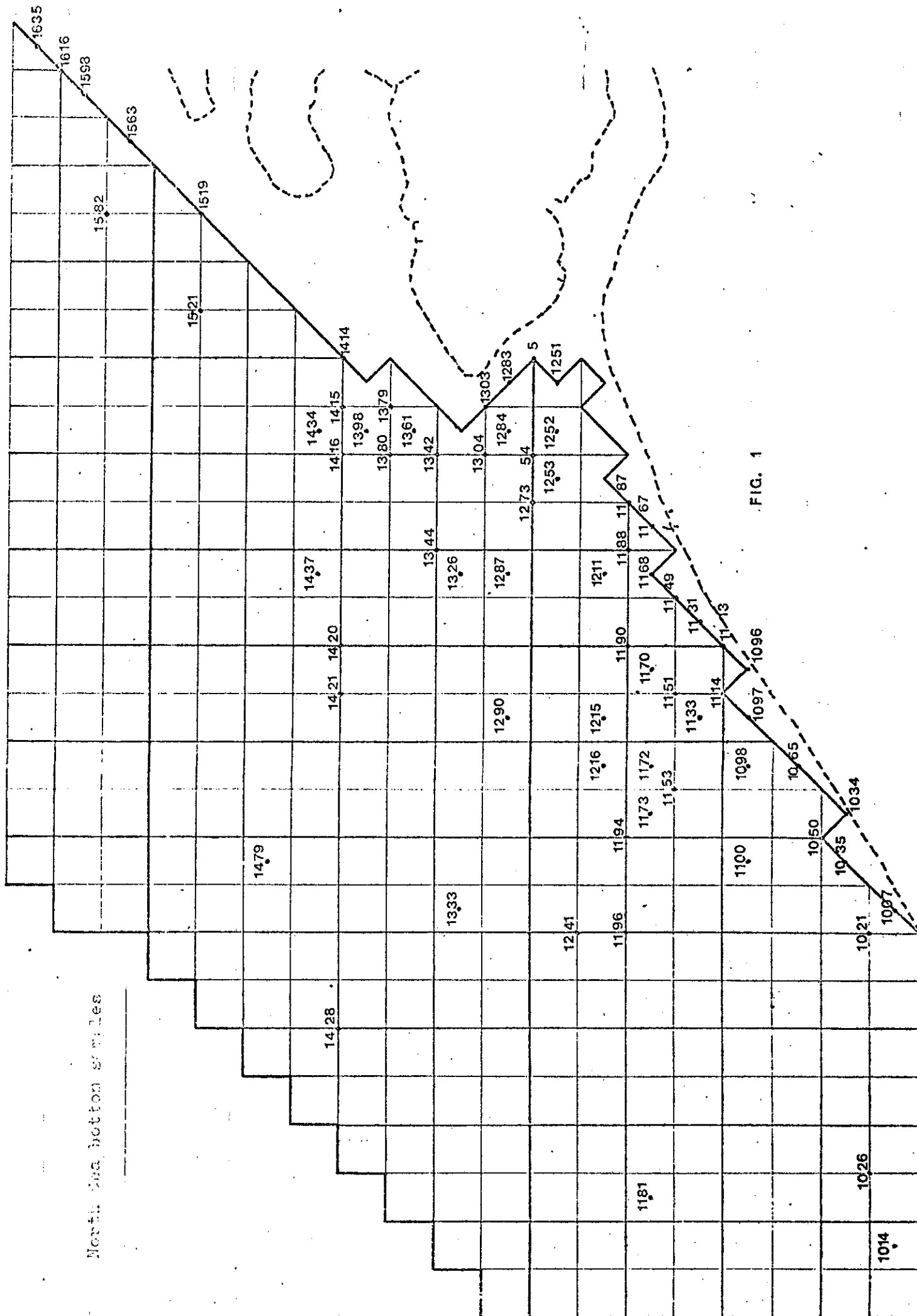


FIG. 1

Figures 2, 3 and 4 show the capacity (Q) of the specimens with respect to the various elements. The capacity of most specimens has been determined by means of the fraction $< 150 \mu$. For some sand-containing specimens we were forced to apply fraction $< 300 \mu$ because, otherwise, we would have had no material left. These latter mostly present much lower capacity values.

A comparison of the capacity between the various elements has taught us that we may classify the elements in the following order of decreasing capacity with respect to soil specimens :



There is a definite difference between monovalent and bivalent radioisotopes where their capacities are concerned. While with Cs, Co and Cd the capacities of sandy samples are small ($< 0,1 \text{ meq/g}$), they remain for all samples with Mn $> 0.6 \text{ meq/g}$. This shows that with Mn there is surely another phenomenon than the exchange of ions. With Co we determine the largest relative dispersion of the capacity values and with Cs we find the smallest differences.

These capacity values do not offer an accurate picture of what may actually take place on the ocean bottom. They only offer the possibility to fix specific elements under extreme conditions (1N solution !) from the sediment.

Figures 5, 6, 7 and 8 show distribution constants (Kd). The following indications have been used : \circ fraction $< 150 \mu$ and \times fraction $< 300 \mu$ of the specimen.

These distribution constants offer a truer picture of what may occur in seawater upon contact with sediments. They have been determined in seawater and with respect to the element in tracer quantities. They show the distribution of the element concerned between the solid and the fluid phase.

The coefficients of distribution determined in sea-water show the following picture for the various radioisotopes :



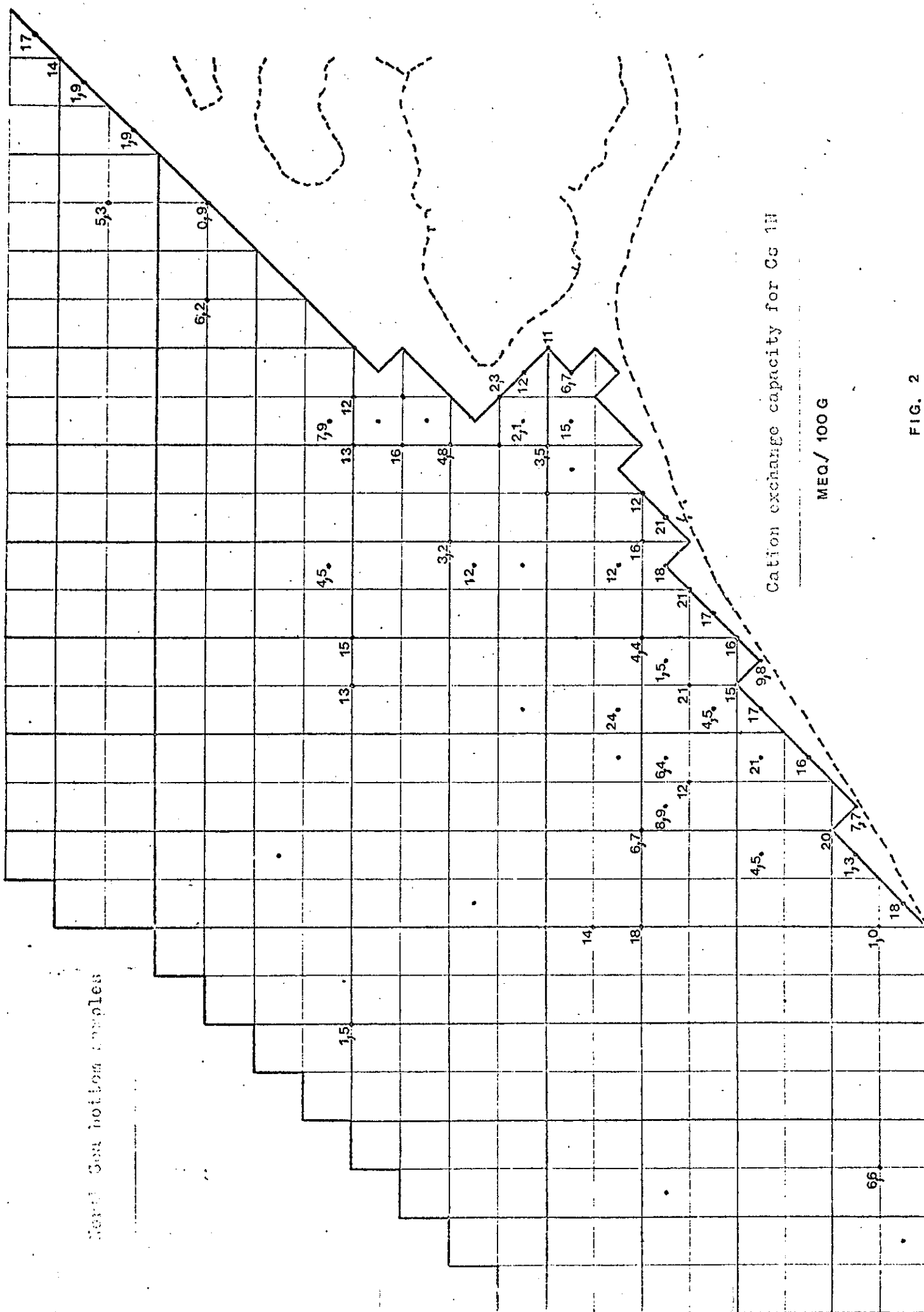


Fig. 2

North Sea bottom samples

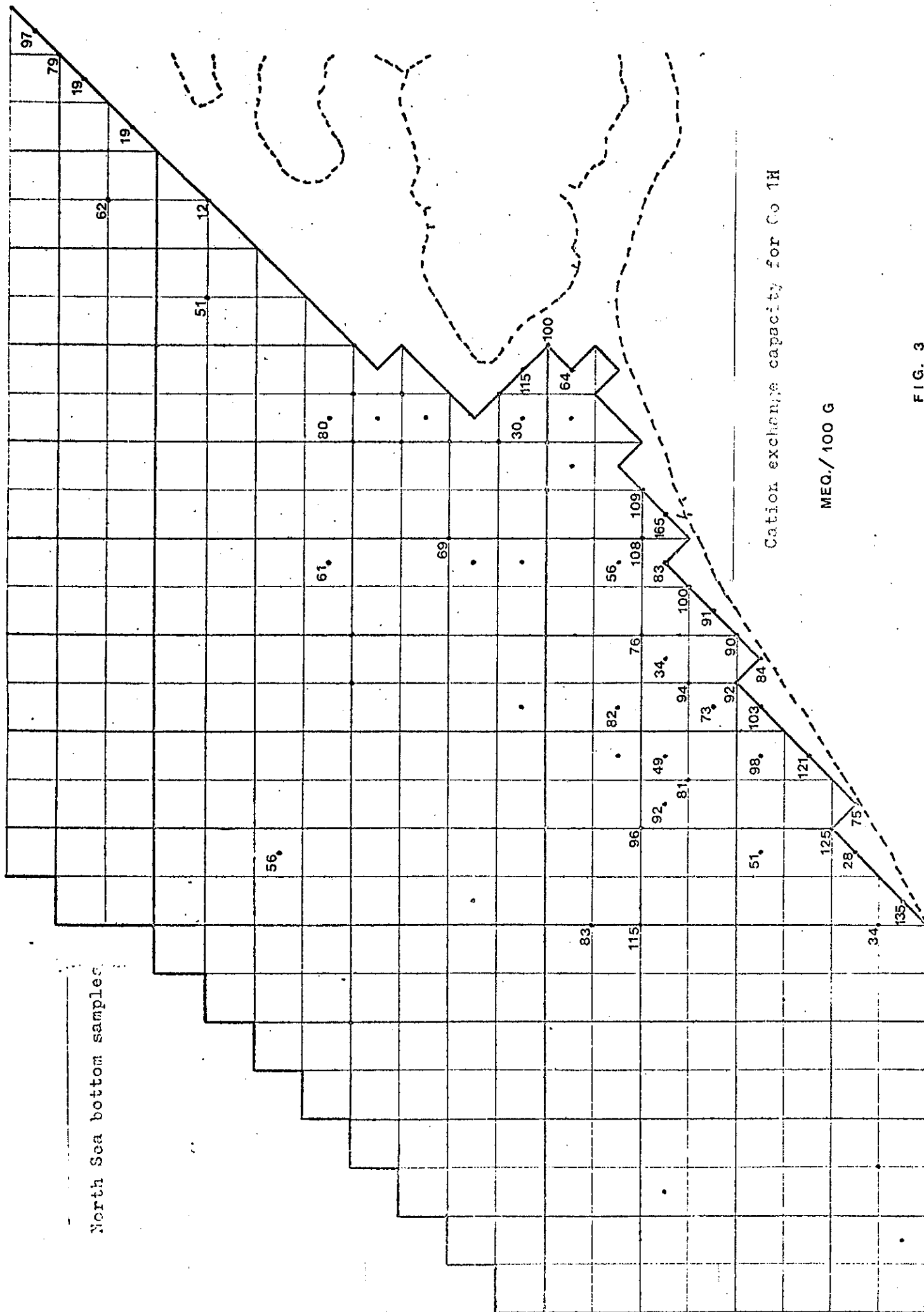


FIG. 3

North Sea bottom samples

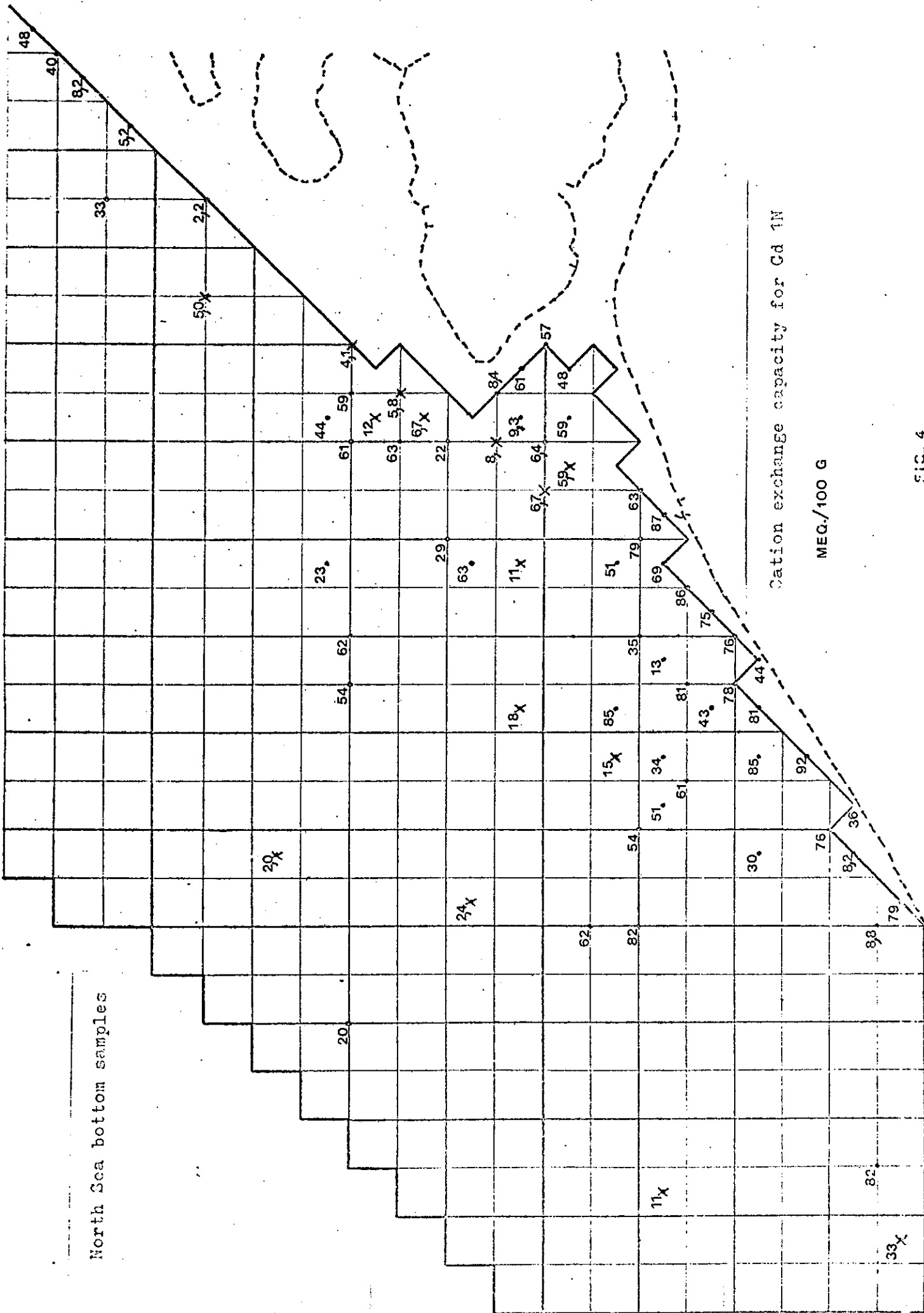


FIG. 4

With all ions we determine for definitely sandy samples small K_d values ($K_d < 50$), while for samples rich in clay and silt these values increase to 100 with Mn and Cd, and to 600 with Co and Cs. Considering the number of specimens examined and the considerable differences in soil structure, it will remain impossible, however, to indicate areas on the maps. This explains why the maps show but the value determined at that specific point.

North Sea bottom samples

Sample ID	X-Coordinate (approx.)	Y-Coordinate (approx.)
97.	100	100
21	150	100
46	200	100
230	250	100
500	300	100
49	150	250
6.4	180	250
19	350	250
70.	300	350
43 x	350	350
36 x	380	350
49 x	400	350
140	400	400
44 x	450	400
54.	480	400
36 x	450	450
39	480	450
33 x	500	450
440.	520	450
130	550	450
300	580	450
51	550	500
320	580	500
330	550	600
480	580	600
270	600	600
660	620	600
490	650	600
690	680	600
300	700	600
360	720	600
450	750	600
320	780	600
510	800	600
140	820	600
36	850	600
500	880	600
93.	800	700
490	820	700
210	850	700
180	880	700
36 x	850	800
690.	880	800
76	900	800
35	920	800
580	950	800
140	980	800
180	1000	800
430	1020	800
220	1050	800
200	1080	800
400	1100	800
120	1150	800
13.	1200	800
72 x	1250	800
380.	1300	800
100	1350	800
95.	1400	800
300	1450	800
560	1480	800
95 x	1500	900
330.	1500	1000
90 x	1500	1100

Kd for Cs¹³⁷

ML/G

ML/G

FIG. 5

North Sea Bottom samples

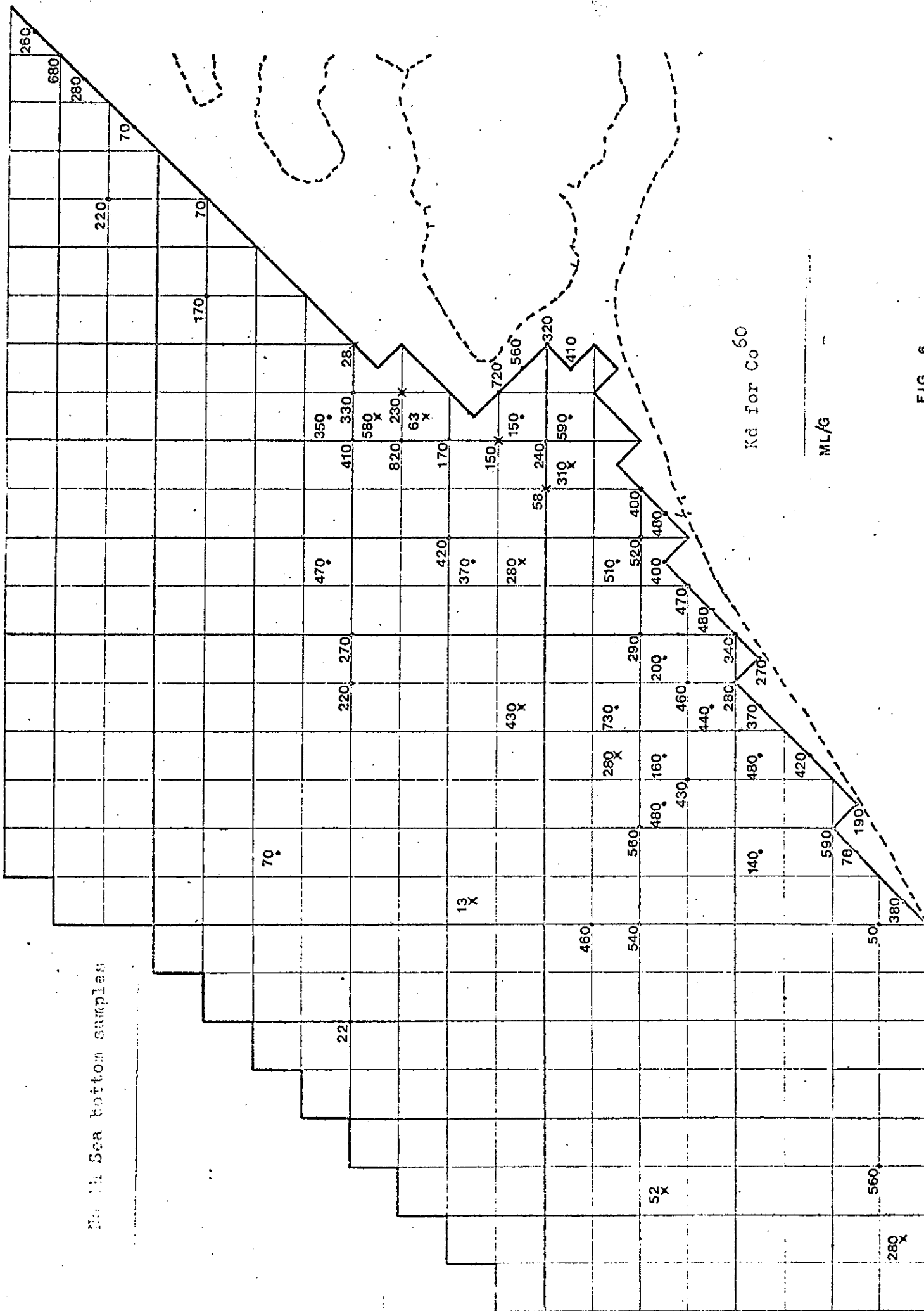


FIG. 6

North Sea bottom samples

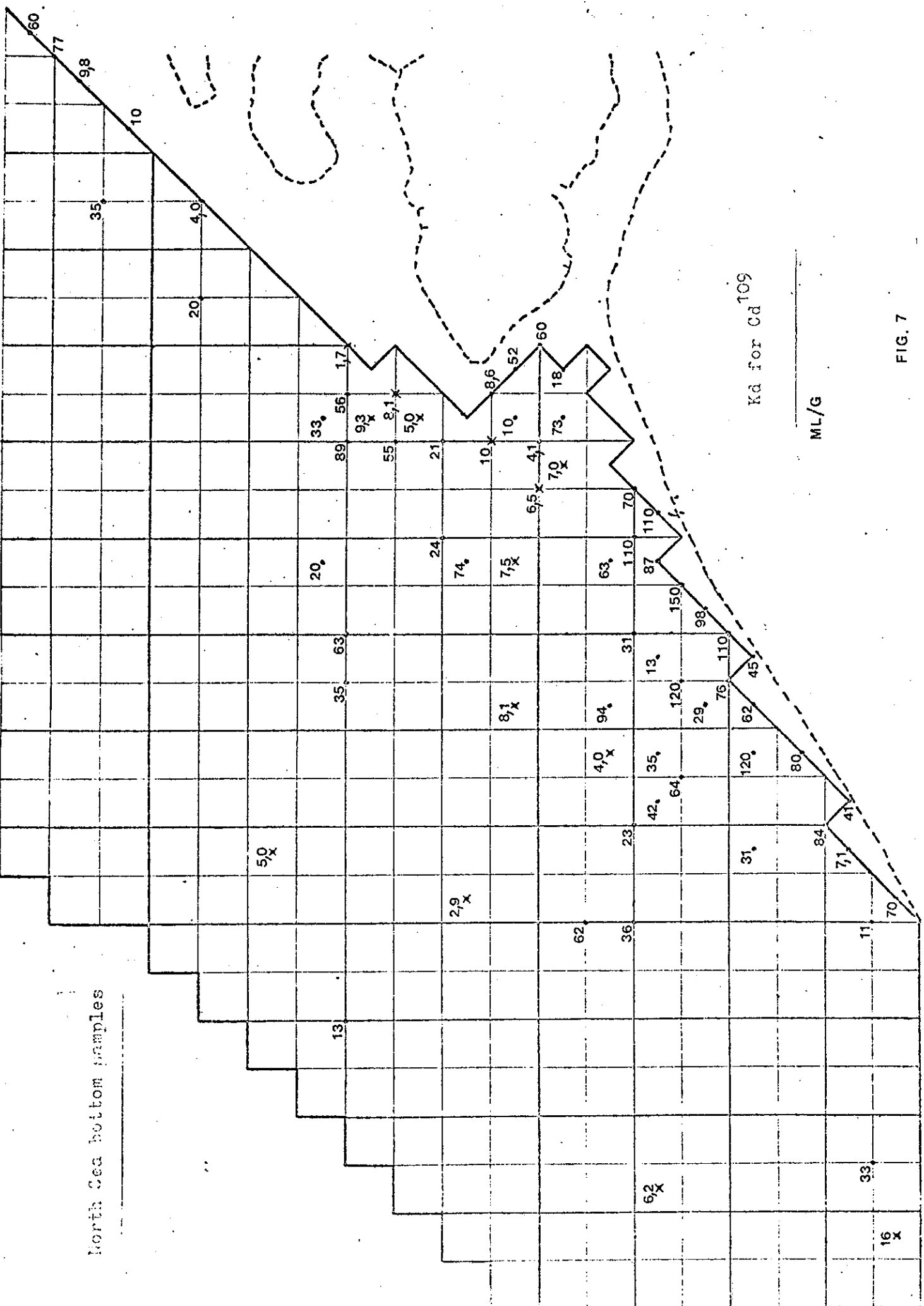


FIG. 7

North Sea bottom samples

Kd for Mn⁵⁴
ml/g

fig. 8

The figure is a grid map of the North Sea bottom samples. The grid is composed of squares, with some squares containing numerical data points. A dashed line represents a boundary or coastline. The data points are as follows:

Sample Number	Location (Approximate Grid Coordinates)
16 _x	(10, 10)
19	(10, 20)
19 _x	(10, 30)
23	(10, 40)
26 _x	(10, 50)
29 _x	(10, 60)
31	(10, 70)
31 _x	(10, 80)
32 _x	(10, 90)
33	(10, 100)
34	(10, 110)
35	(10, 120)
36	(10, 130)
37	(10, 140)
38	(10, 150)
39	(10, 160)
40	(10, 170)
41	(10, 180)
42	(10, 190)
43	(10, 200)
44	(10, 210)
45	(10, 220)
46	(10, 230)
47	(10, 240)
48	(10, 250)
49	(10, 260)
50	(10, 270)
51	(10, 280)
52	(10, 290)
53	(10, 300)
54	(10, 310)
55	(10, 320)
56	(10, 330)
57	(10, 340)
58	(10, 350)
59	(10, 360)
60	(10, 370)
61	(10, 380)
62	(10, 390)
63	(10, 400)
64	(10, 410)
65	(10, 420)
66	(10, 430)
67	(10, 440)
68	(10, 450)
69	(10, 460)
70	(10, 470)
71	(10, 480)
72	(10, 490)
73	(10, 500)
74	(10, 510)
75	(10, 520)
76	(10, 530)
77	(10, 540)
78	(10, 550)
79	(10, 560)
80	(10, 570)
81	(10, 580)
82	(10, 590)
83	(10, 600)
84	(10, 610)
85	(10, 620)
86	(10, 630)
87	(10, 640)
88	(10, 650)
89	(10, 660)
90	(10, 670)
91	(10, 680)
92	(10, 690)
93	(10, 700)
94	(10, 710)
95	(10, 720)
96	(10, 730)
97	(10, 740)
98	(10, 750)
99	(10, 760)
100	(10, 770)

8.
i

When we compare the values measured with regard to capacity and K_d for one and the same ion, we note a certain connection determined between both quantities only with Cs and Cd (fig. 9, 10). With Co and Mn there actually seems to be no connection (fig. 11, 12). Investigations conducted by Duursma (*) on soil samples from all over the world lead to the same result where Cs is concerned. They determine a connection with Zn, too.

Our determinations with Zn^{65} are still being conducted but already they point in this direction, too. He did not investigate Cd^{109} .

We also find a certain correlation to exist between the capacity and the K_d determined with Cd and Cs for one and the same sample. Duursma, too, determines no connection between K_d and Q with Co and Mn. For this reason and based on sorption reaction speed determinations he concludes that there can be an exchange of ions only with Cs and Zn while different mechanisms play a more important part for the other radioisotopes (precipitation, isotopic exchange, complex formation ...). The speed of the sorption reaction which supplies an indication for the sorption mechanism will be further investigated in order to check the possibilities proposed by Duursma.

The influence of other ions (Na, K, Ca and Mg) on the sorption of Cd, Co and Mn was investigated. While with Cs (cfr. 1973/Sed.-Synthesis 01) it was mostly Na and K that caused a significant decrease of K_d whereas Ca and Mg had lesser influence, conditions are different where bivalent radioisotopes are concerned. With Cd^{109} the differences between monovalent and bivalent ions are much less pronounced. Ca and Mg have a greater influence here as compared to Na and K. We have the same picture again with the sorption of Mn^{54} and Co^{60} where the influence of Na and K is considerably decreased (fig. 13, 14, 15).

(*) E.K. Duursma, D. Eisma "Studies concerning Reactions of Radioisotopes with Sediments and Suspended Particles of the Sea". Netherlands Journal of Sea Research 6 (3):265-324 (1973)

Fig. 9

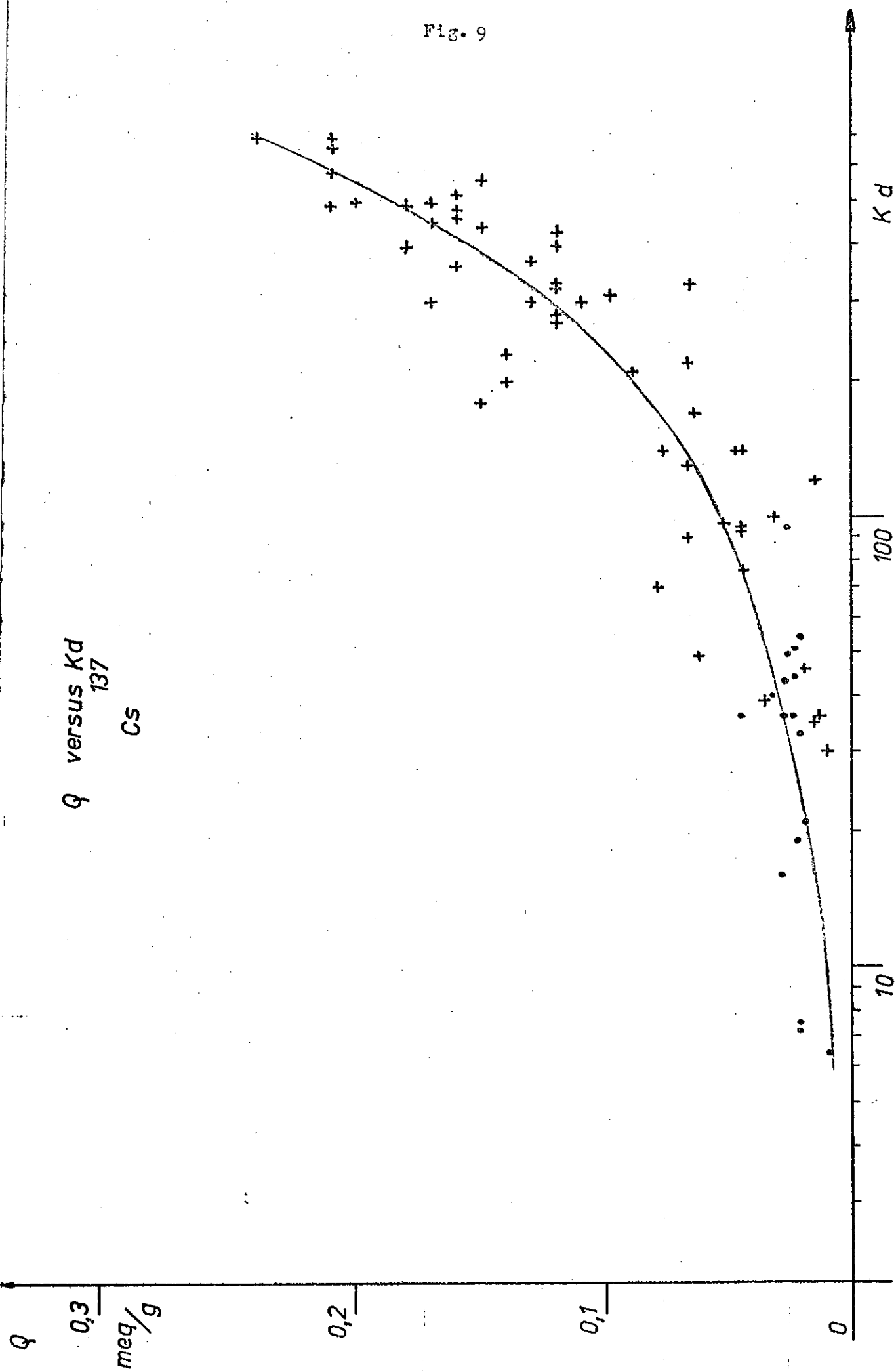


Fig. 10

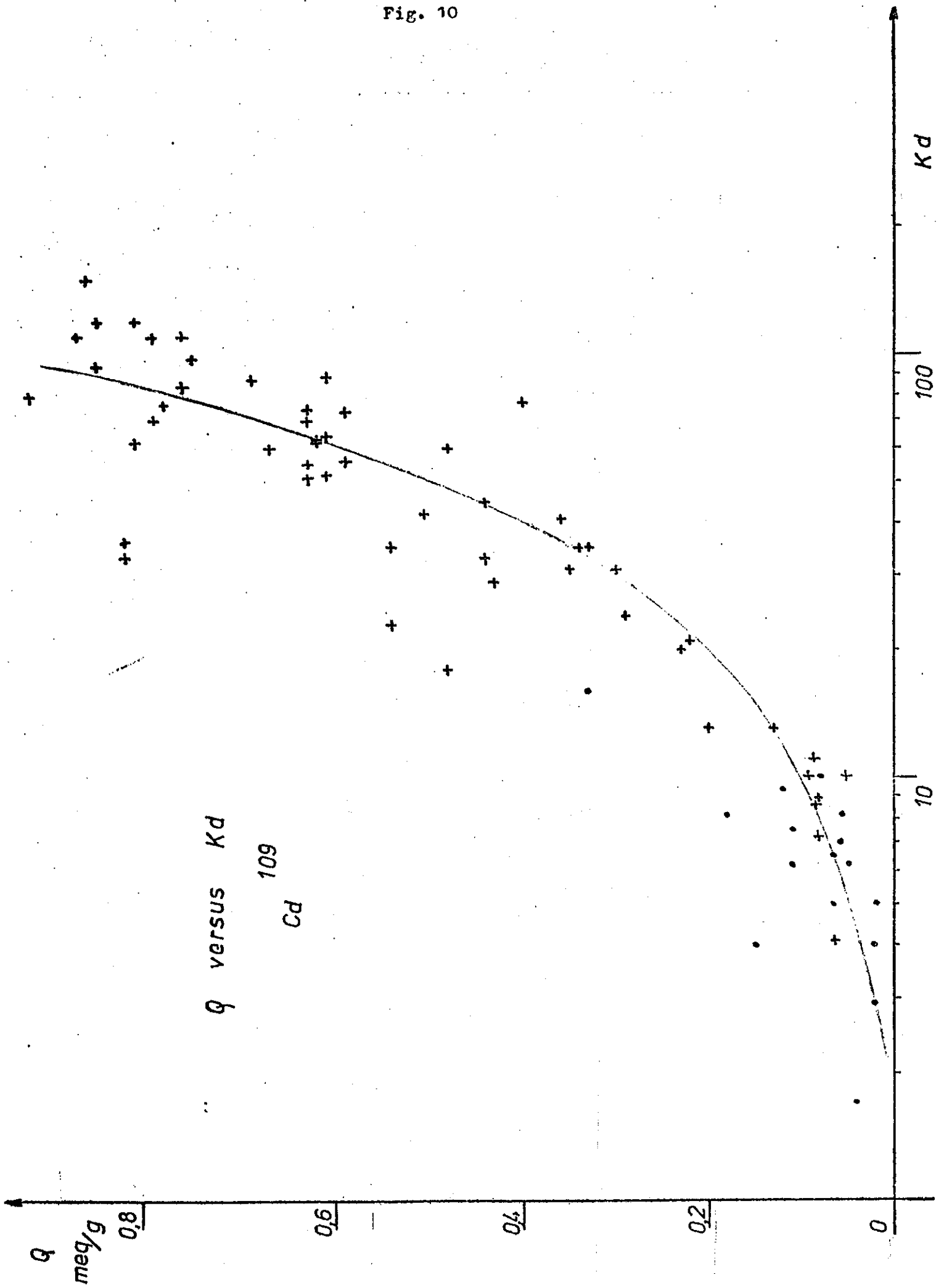


Fig. 11

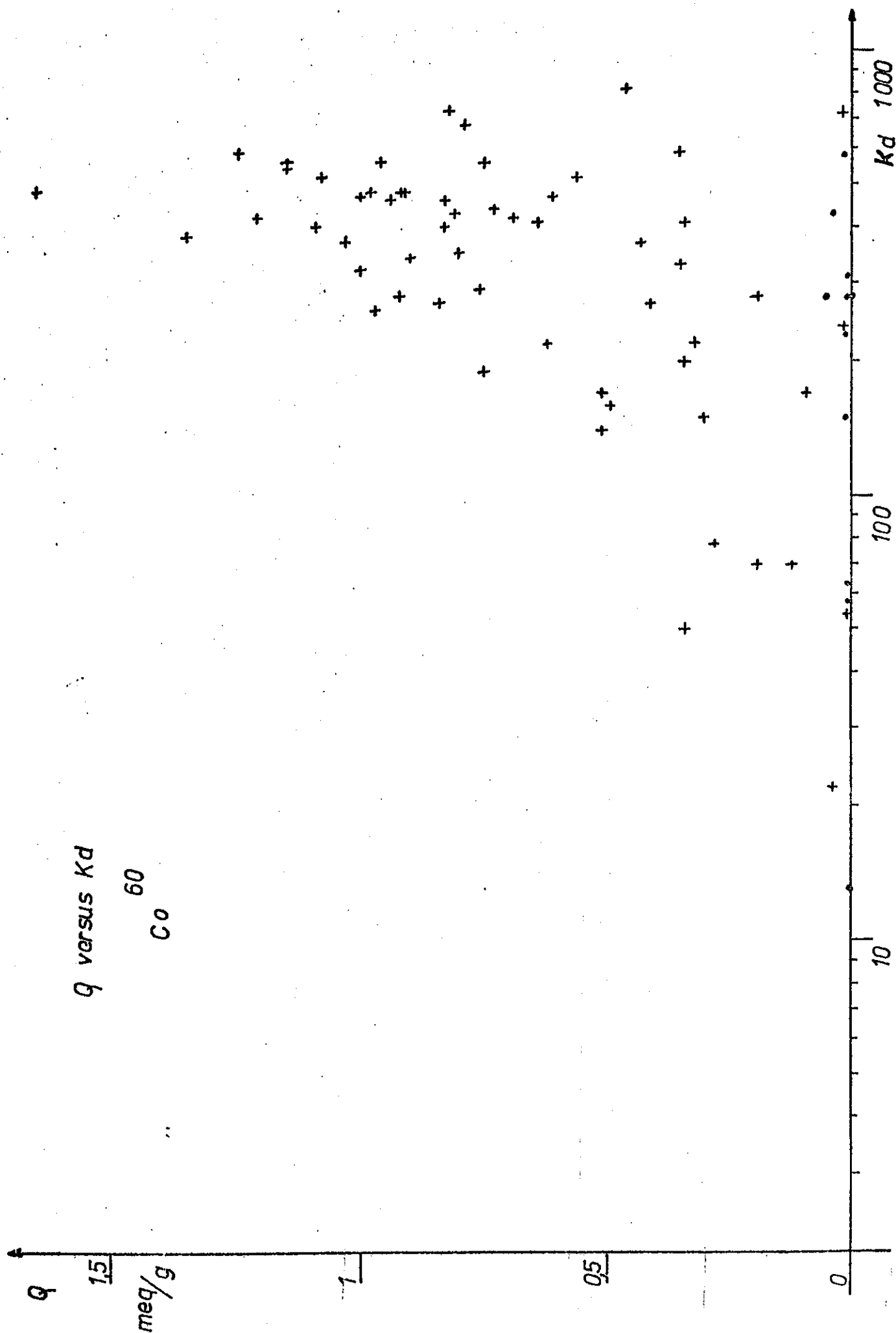


Fig. 12

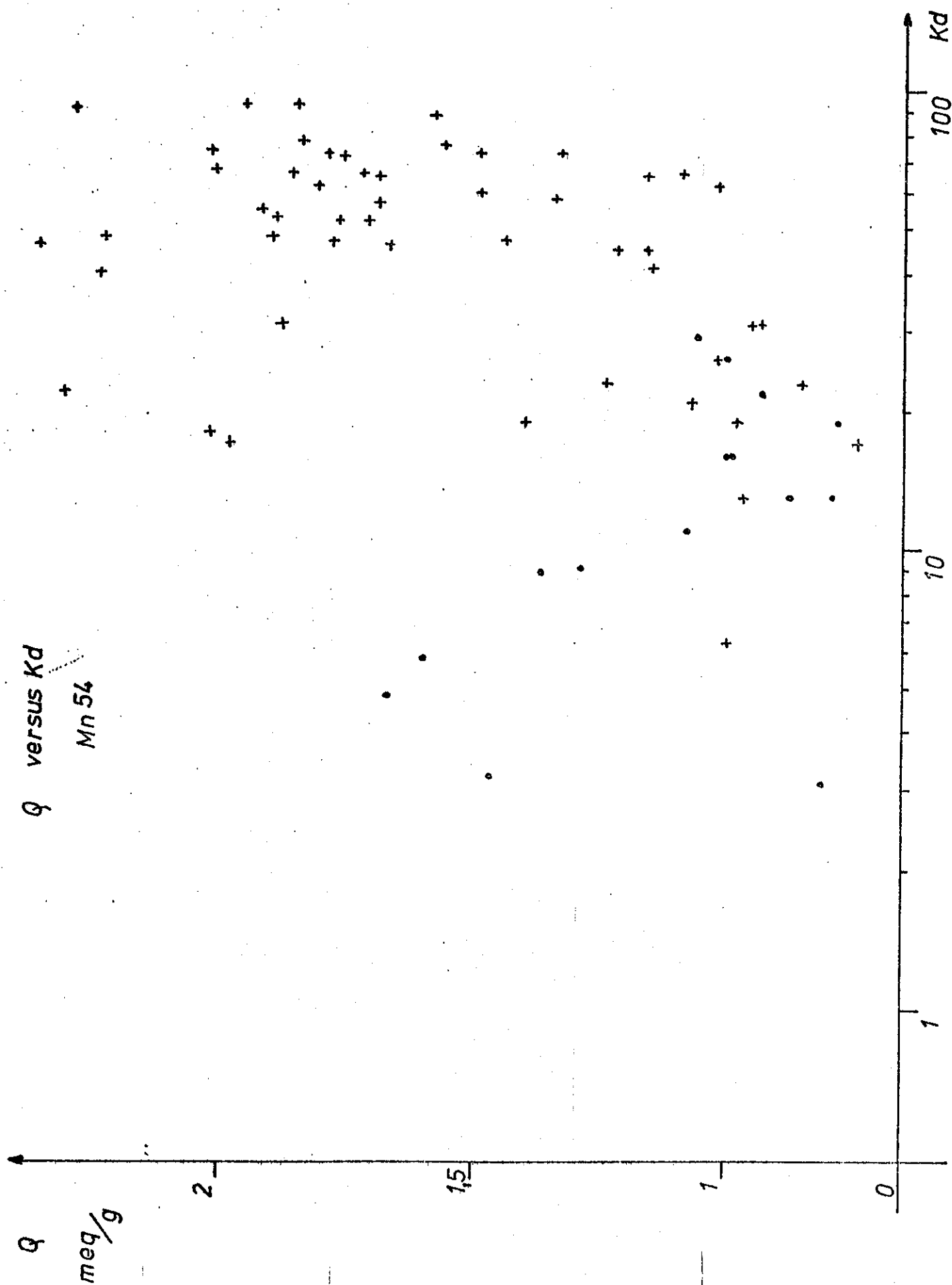


Fig. 13

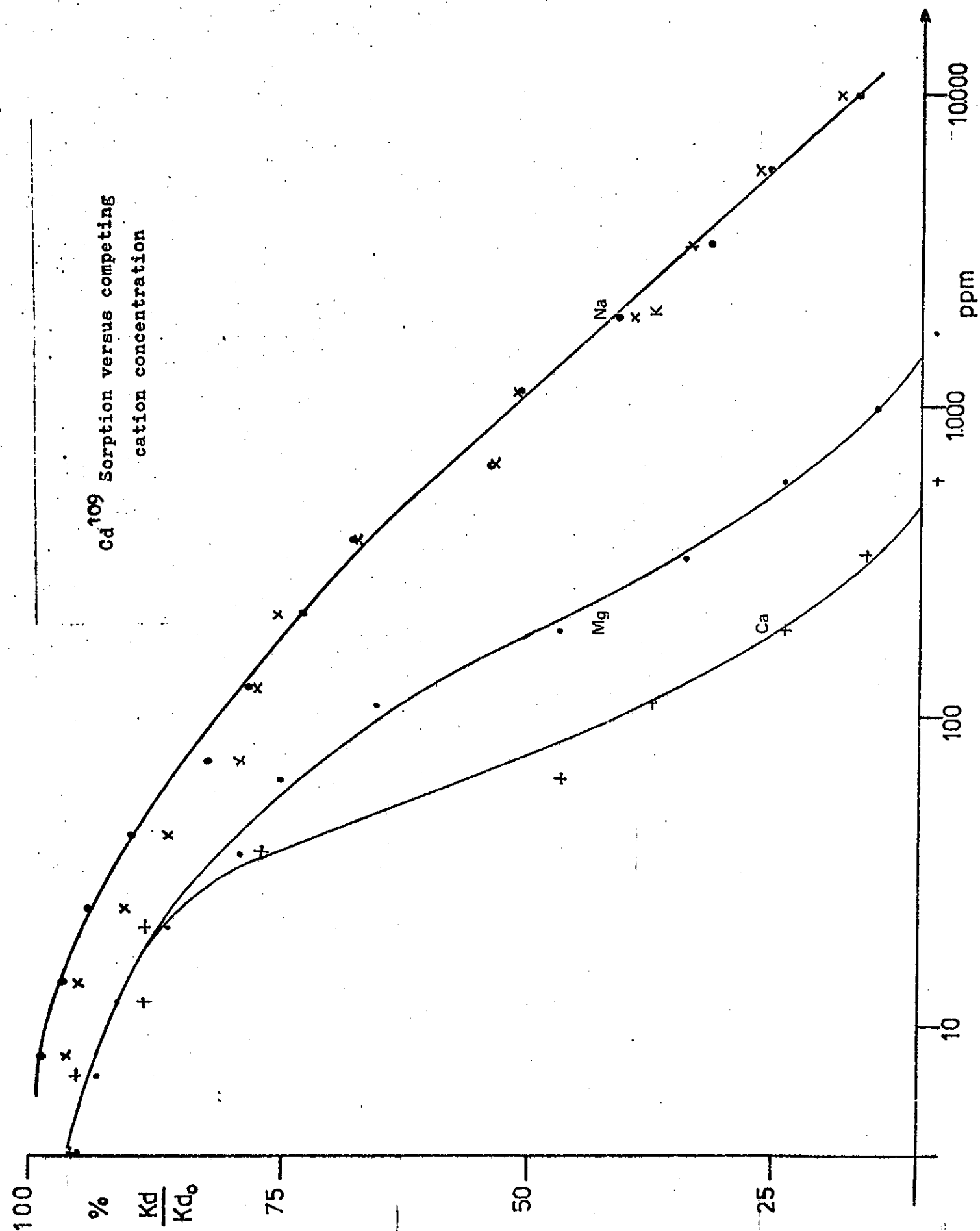


Fig. 14

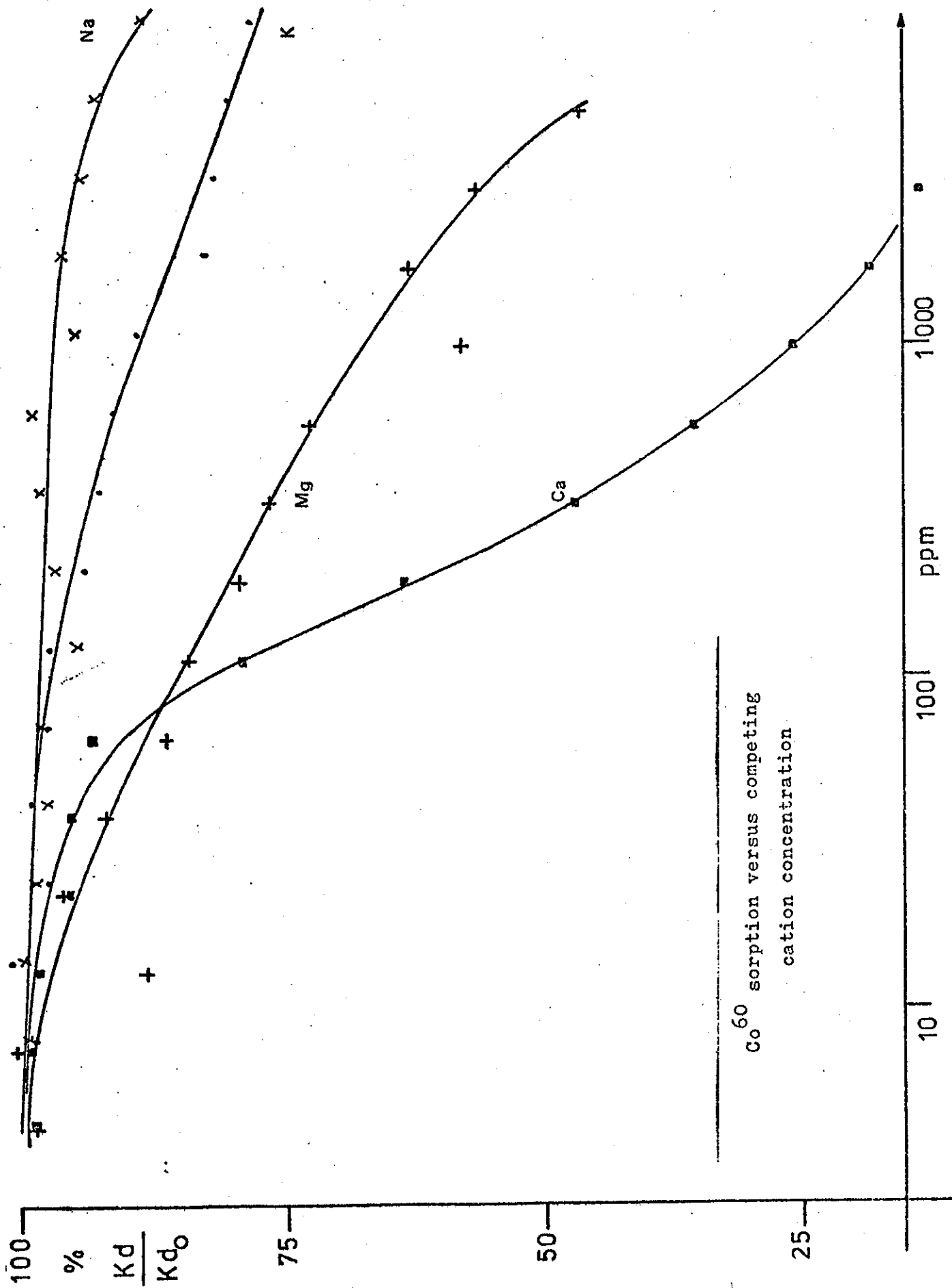
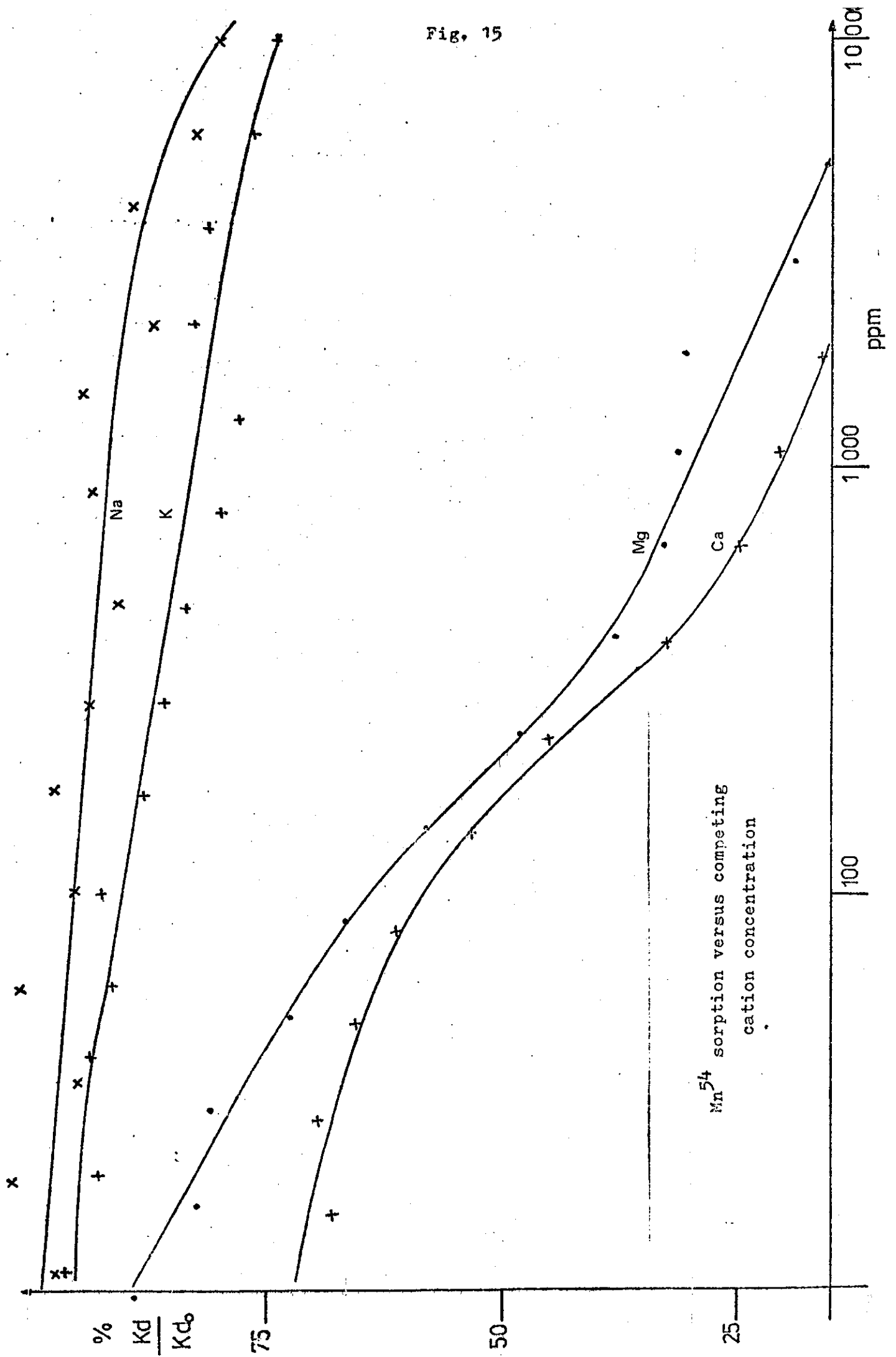


Fig. 15



In order to bridge the gap existing between capacities determined by 1N solution and distribution constants determined by tracer quantities, we determined in seawater the Kd for five specimens with an increasing concentration of the same ion. With Mn⁵⁴, Co⁶⁰ and Cd¹⁰⁹ this influence is much smaller than with Cs¹³⁷ which also points to other reaction mechanism than a pure exchange of ions. (fig. 16,17,18,19)

There will be further investigation to determine a possible connection with the granulometric data of the soil samples as collected by Prof. Gullentops' research team. The average diameter as well as the quantity of clay and silt in the samples appear to be the most appropriate parameters for this purpose. Other investigations will determine possible influence by the lime contents and by the organic material.

The tests proposed and worked out by Duursma for the purpose of determining the cleaning effect produced by suspensions on the radioactive solutions and the pertaining values of Kd will also be conducted in the future where samples rich in clay and silt are concerned. He draws, however, attention to the fact that Kd values obtained by means of different methods may mutually vary to a greater extent as compared to those obtained with one and the same method applied to different samples. He suggests, consequently, to use Kd values of these tests that best agree with what occurs in nature. Thus the results obtained with the precipitation will be more appropriate for describing the absorption of ions by soil material which has been brought again into a state of suspension and subsequently precipitates. Also, the thin layer method will be more appropriate in conditions where a simple contact exists between the water and the sediments without having these latter return to a state of suspension.

Fig.16

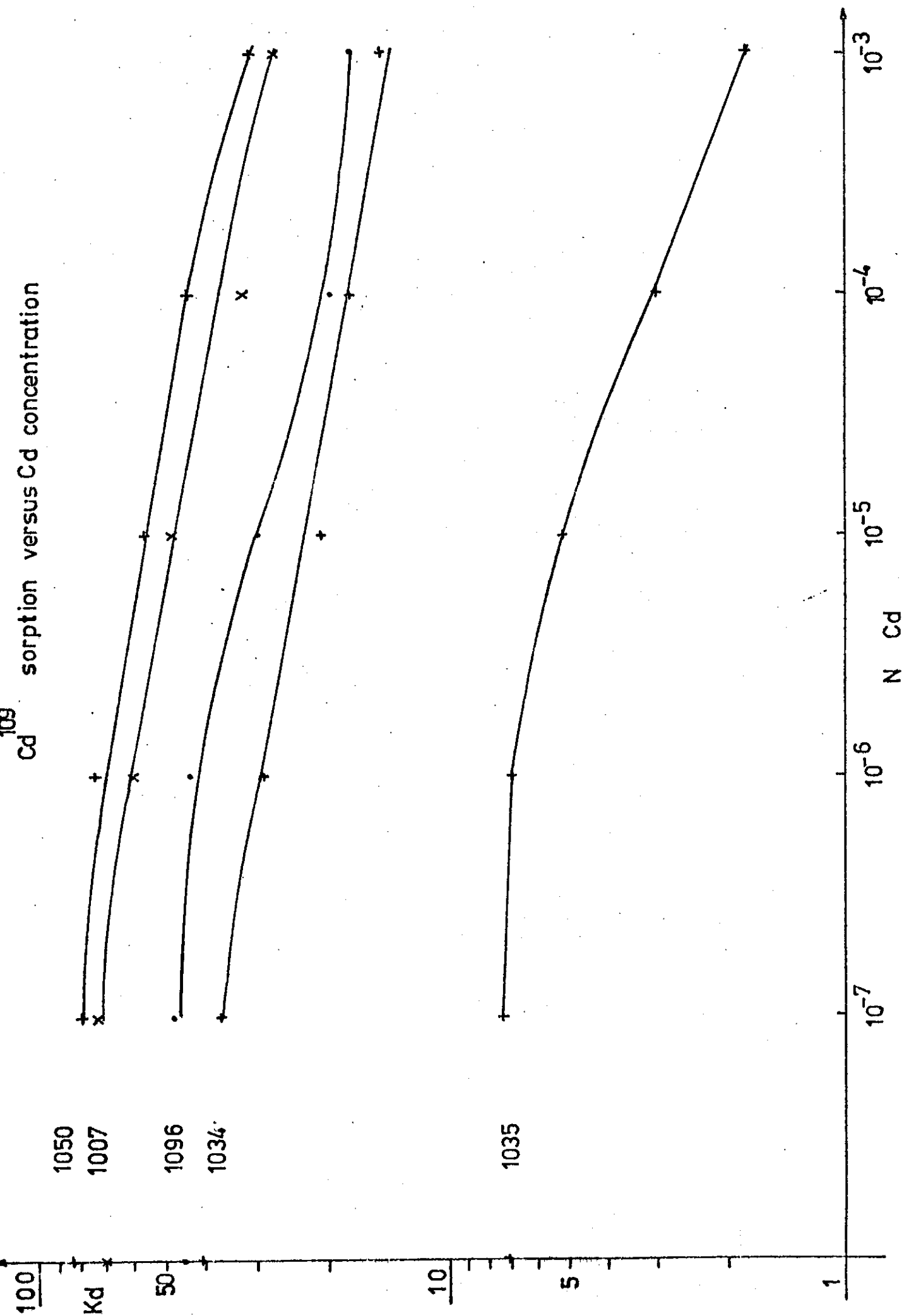


Fig. 17

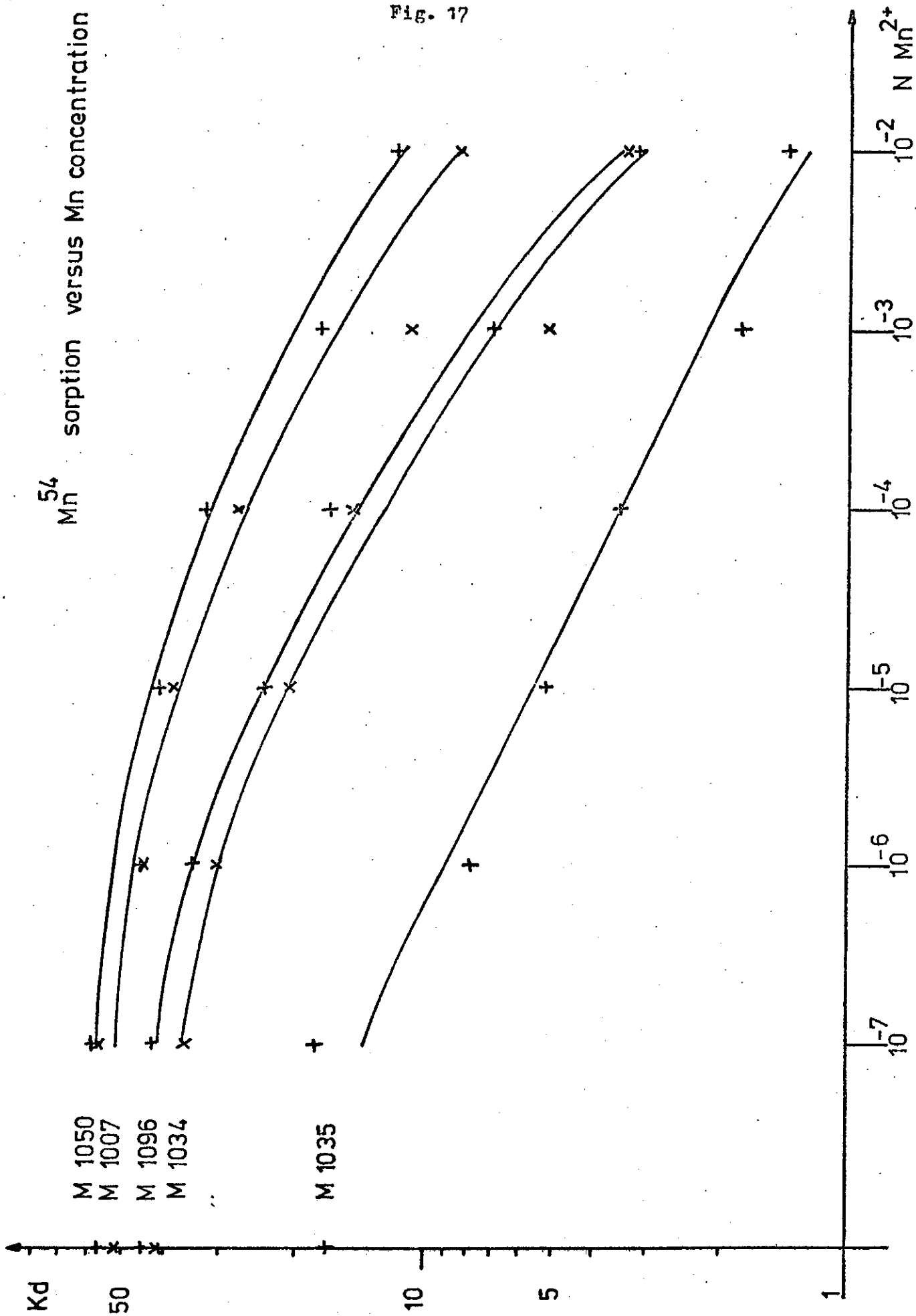


Fig.18

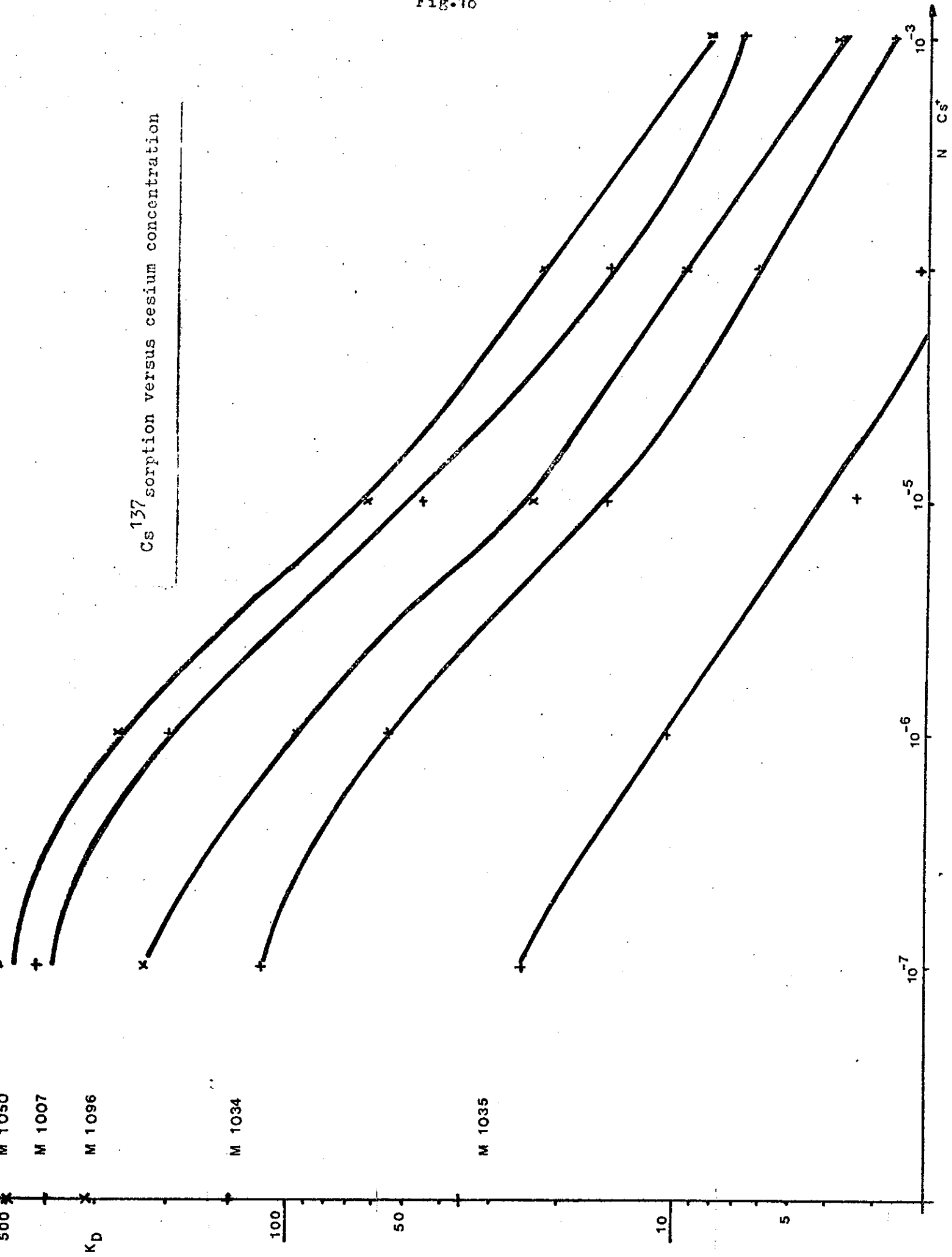


Fig. 19

^{60}Co sorption versus cobalt concentration

M 1050

M 1007

M 1096

M 1034

M 1035

K_d

500

100

50

10

10^{-7}

10^{-6}

10^{-5}

10^{-4}

10^{-3}
N C_0^{2+}

