1761

TECHNICAL REPORT
1974/SED. SYNTHESE 01

Sorption by some North Sea Sediments

II-III
1974

by A.BASTIN and M.MEEUSSEN,
Laboratory of Marine Geology and Recent Sediments,
Institut Royal des Sciences Naturelles de Belgique.

The sorption properties of about seventy soil samples of the thousand points system were investigated up to now by means of four radioisotopes, namely : Cs^{137}, (Cs^{134}), Co^{60}, Mn^{54} and Cd^{109}. Similar tests with Zn^{65} 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 Sea bottom samples

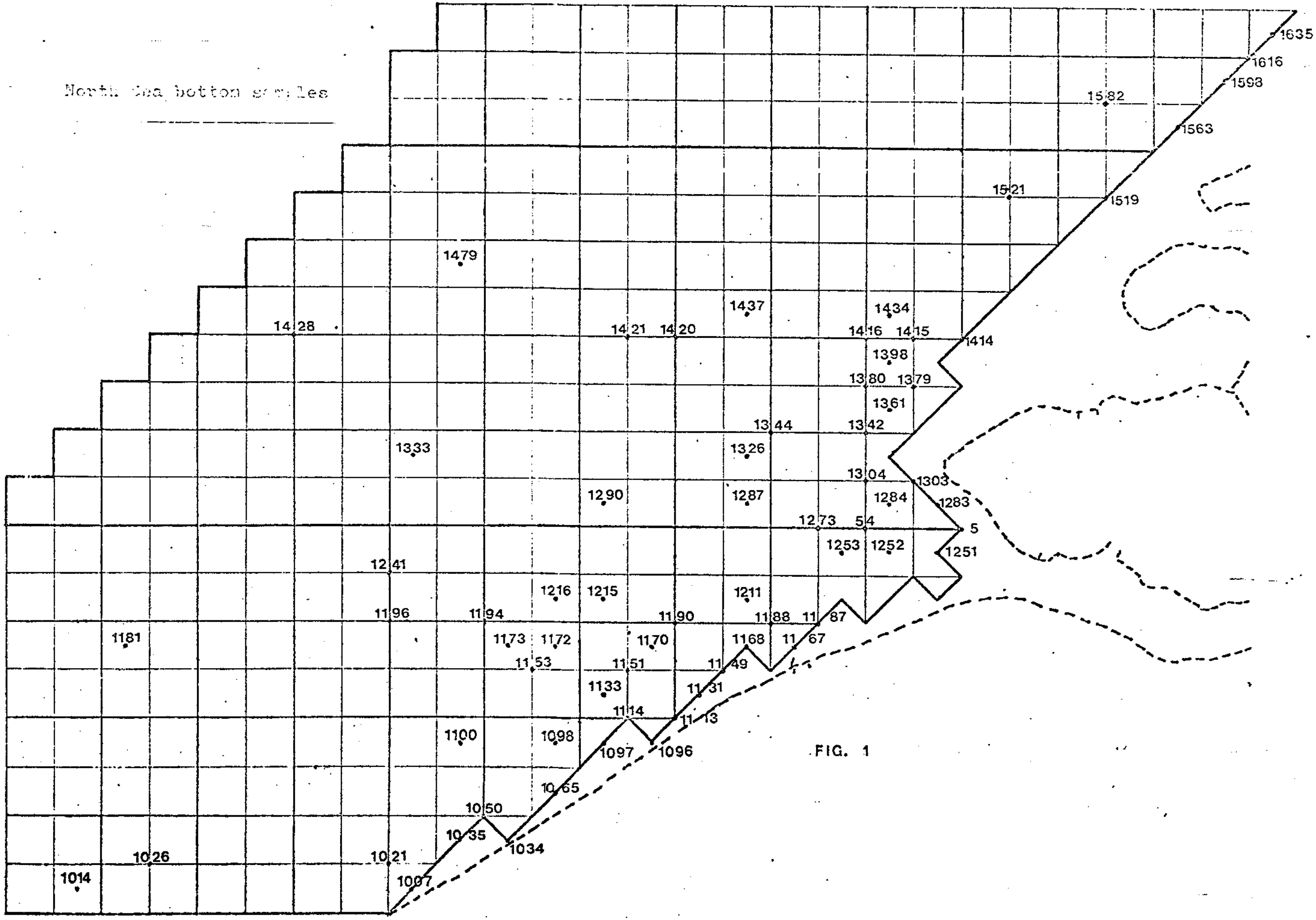


FIG. 1

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 determinded by means of the fraction < 150 µ. For some sand-containing specimens we were forced to apply fraction < 300 µ 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 :

$$Mn \gg Co > Cd \gg Cs$$

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 meq/g), they remain for all samples with Mn >0.6 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.

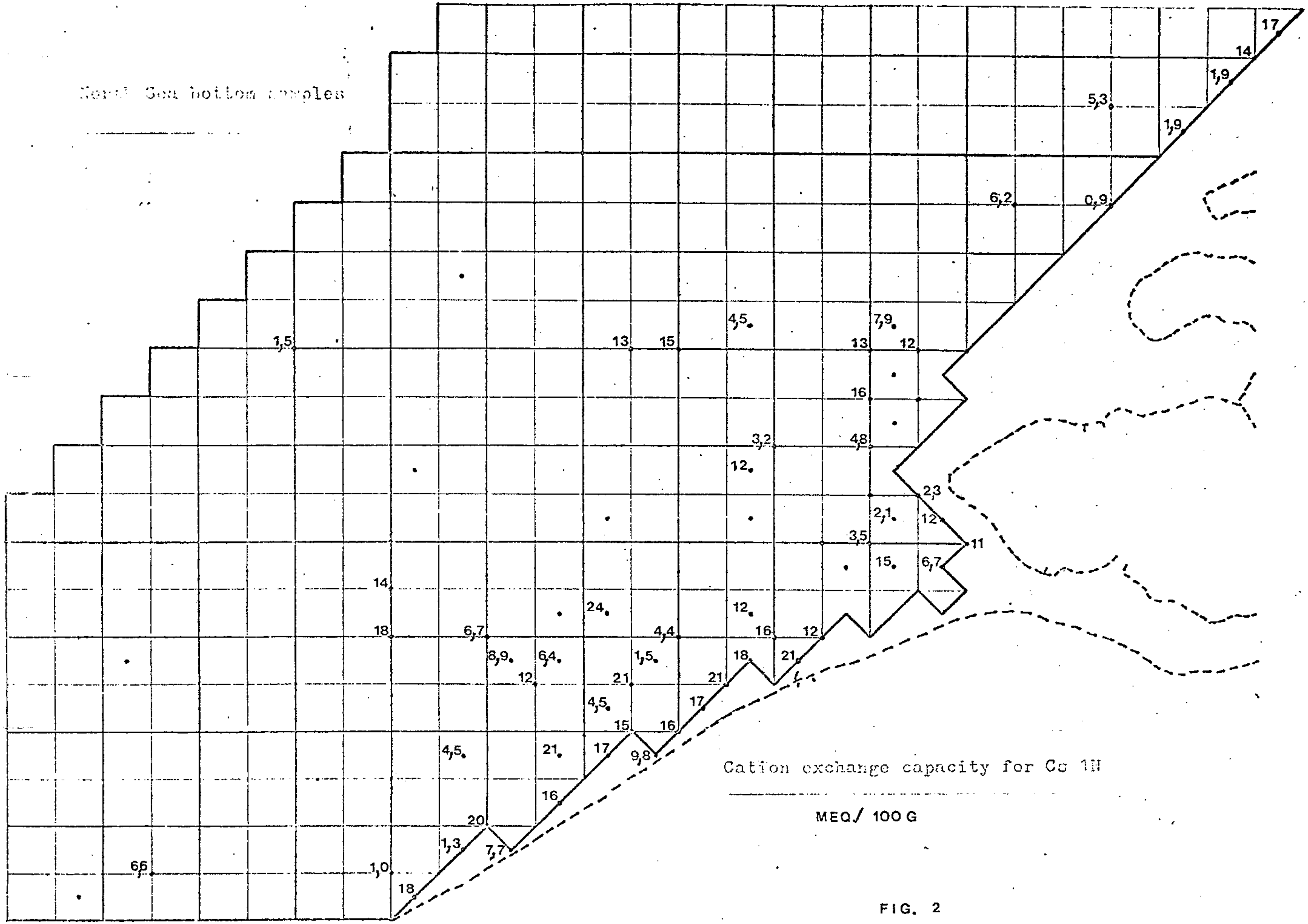
Figures 5, 6, 7 and 8 show distribution constants (Kd). The following indications have been used : °fraction < 150 µ and ˣ fraction < 300 µ of the specimen.

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 coeffi~~ci~~ents of distribution determined in sea-water show the following picture for the various radioisotopes :

$$Co \gg Cs \gg Cd \gg Mn$$

North Sea bottom samples

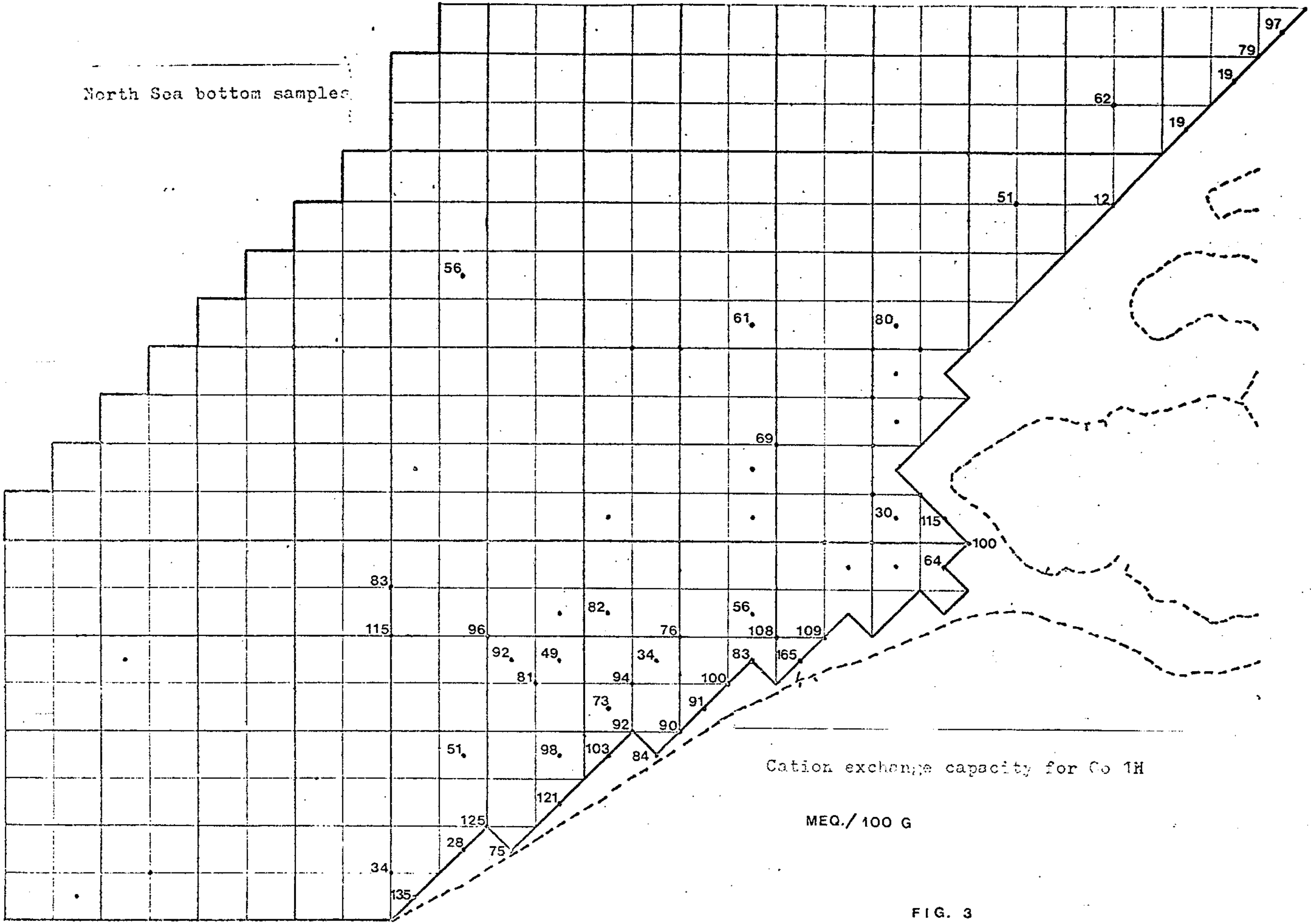


Cation exchange capacity for Cs 1N

MEQ/ 100 G

FIG. 2

North Sea bottom samples



Cation exchange capacity for Co 1H

MEQ./100 G

FIG. 3

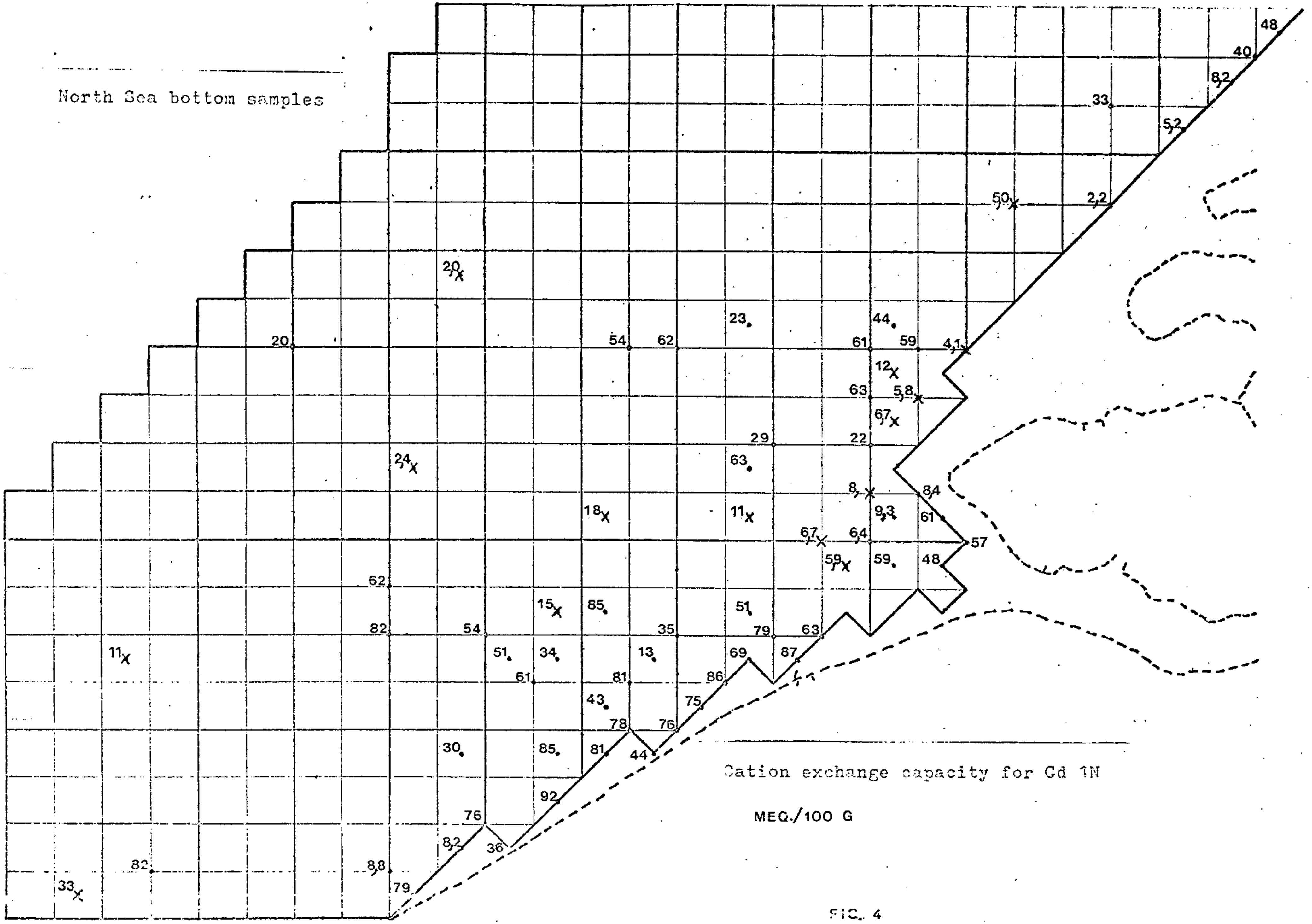
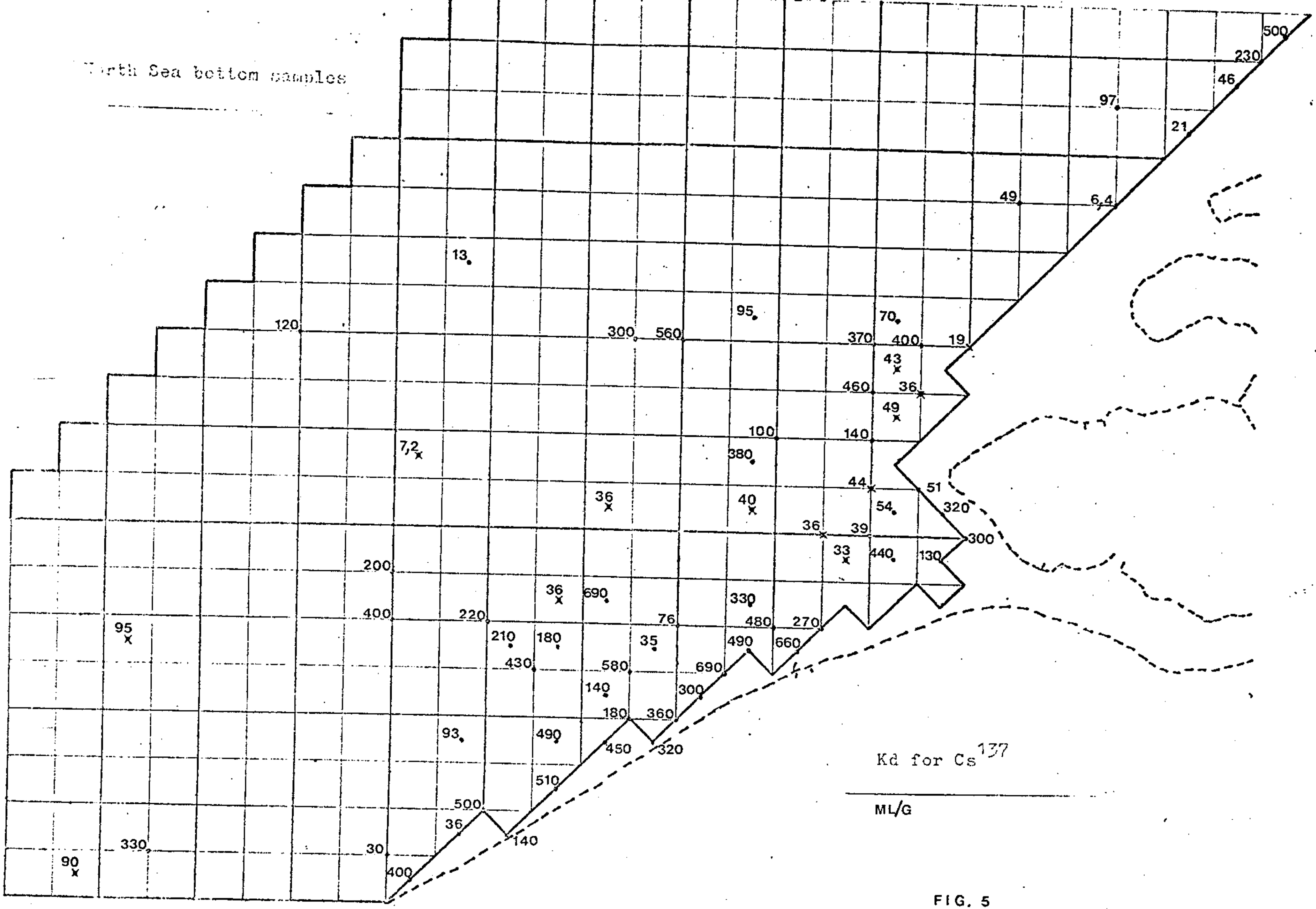

North Sea bottom samples
48
40
8,2
33
5,2
50
2,2
20
23
44
54
62
61
59
4,1
12
63
5,8
67
29
22
24
63
8
8,4
18
11
9,3
61
67
6,4
57
59
59
48
62
15
85
51
82
54
35
79
63
11
51
34
13
69
87
61
81
86
43
75
78
76
30
85
81
44
92
76
8,2
36
82
8,8
33
79
Cation exchange capacity for Cd 1N
MEQ./100 G

FIG. 4

With all ions we determine for definitely sandy samples small Kd values (Kd<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



Kd for Cs^{137}

ML/G

FIG. 5

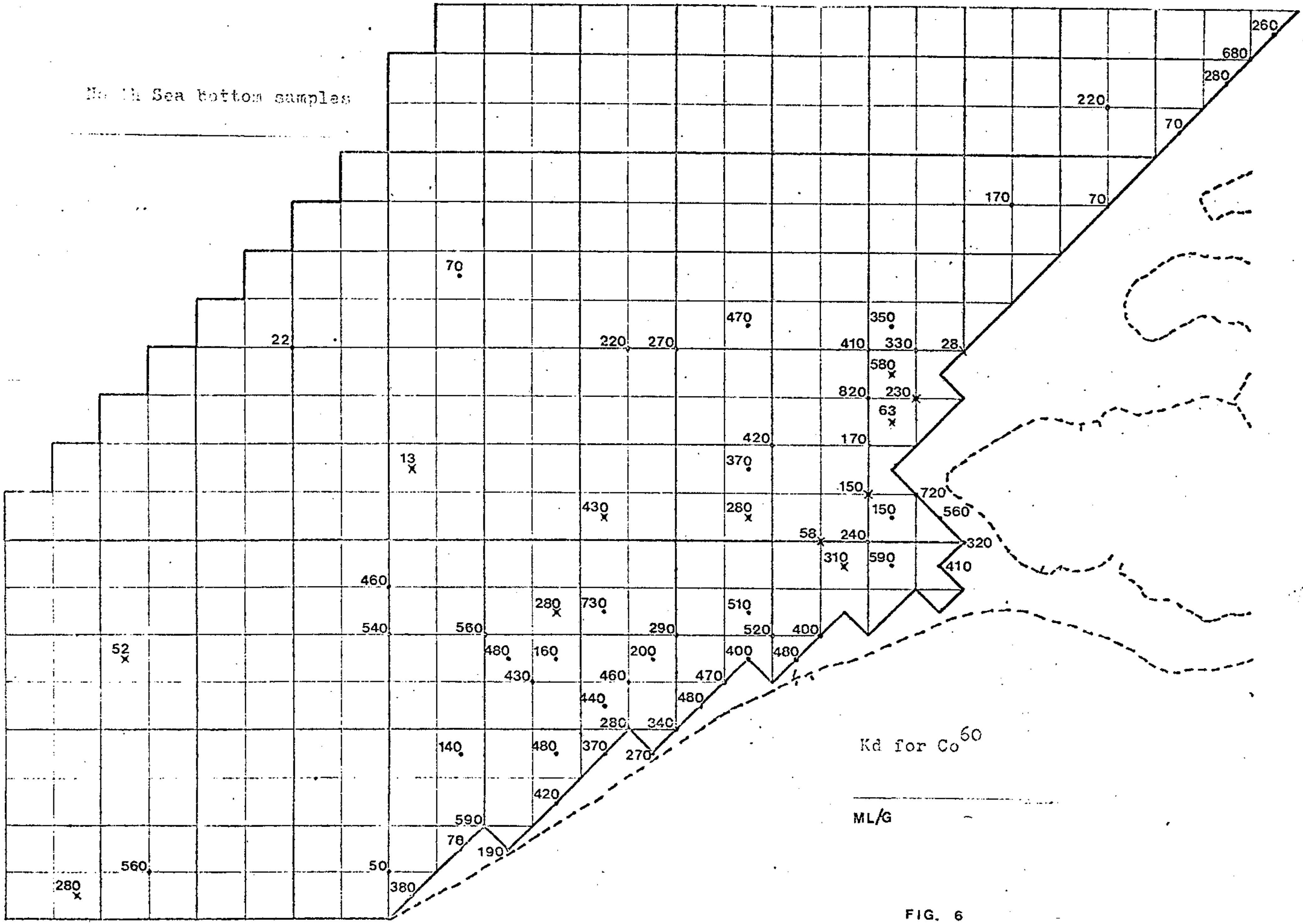
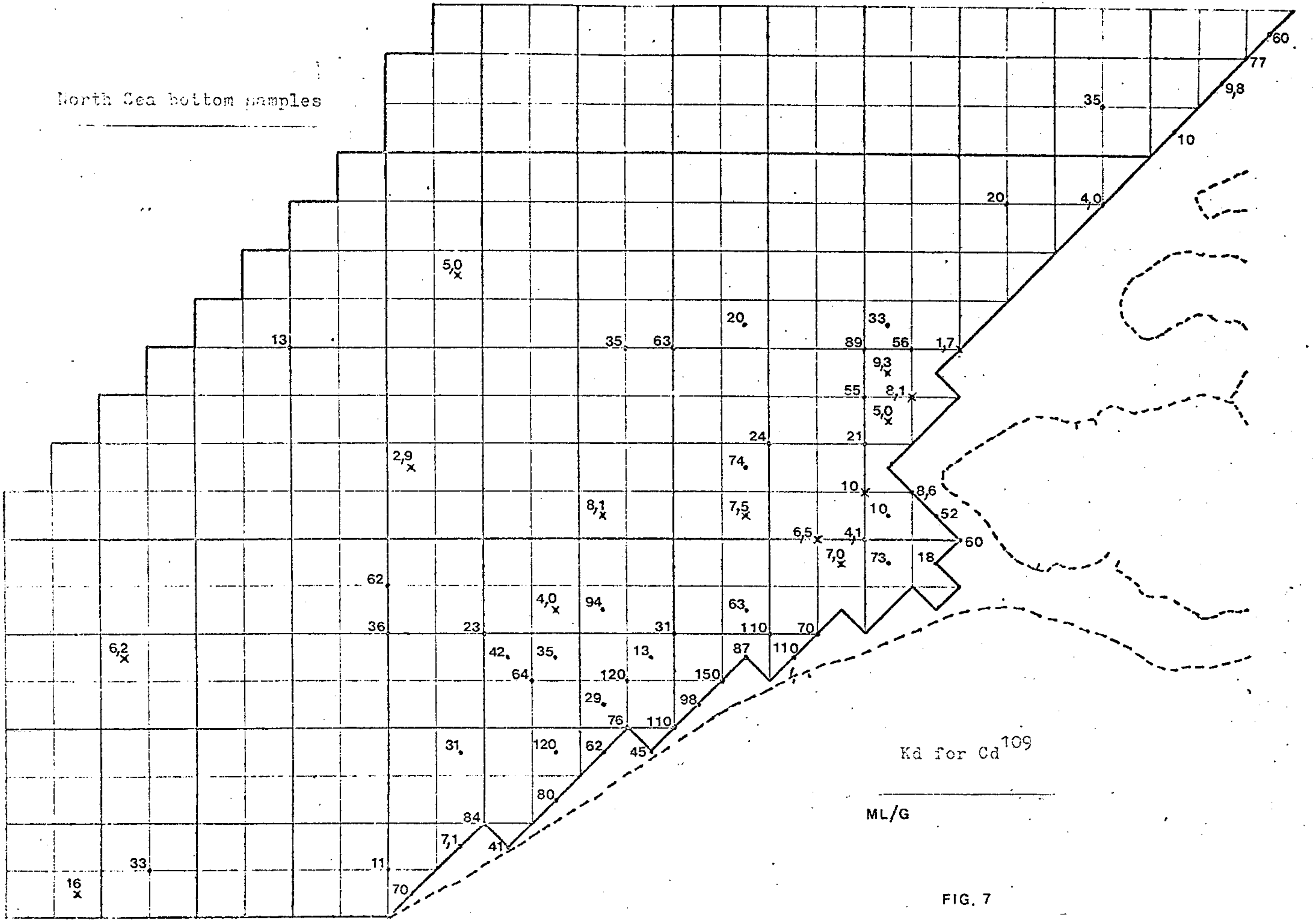


FIG. 6

North Sea bottom samples

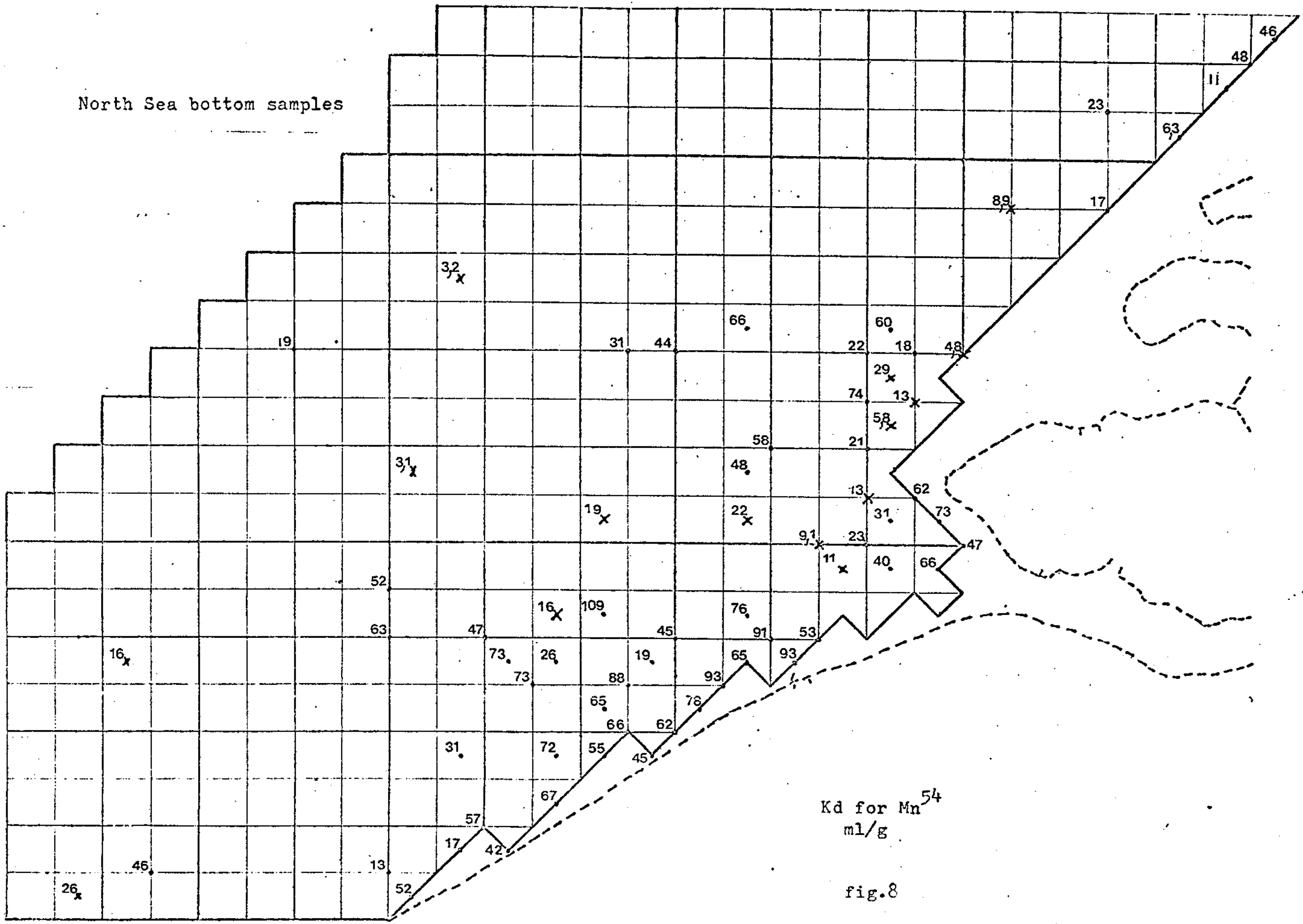


Kd for Cd^{109}

ML/G

FIG. 7

North Sea bottom samples



Kd for Mn^{54}
ml/g

fig.8

When we compare the values measured with regard to capacity and Kd 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 Kd determined with Cd and Cs for one and the same sample. Duursma, too, determines no connection between Kd 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 Kd 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)

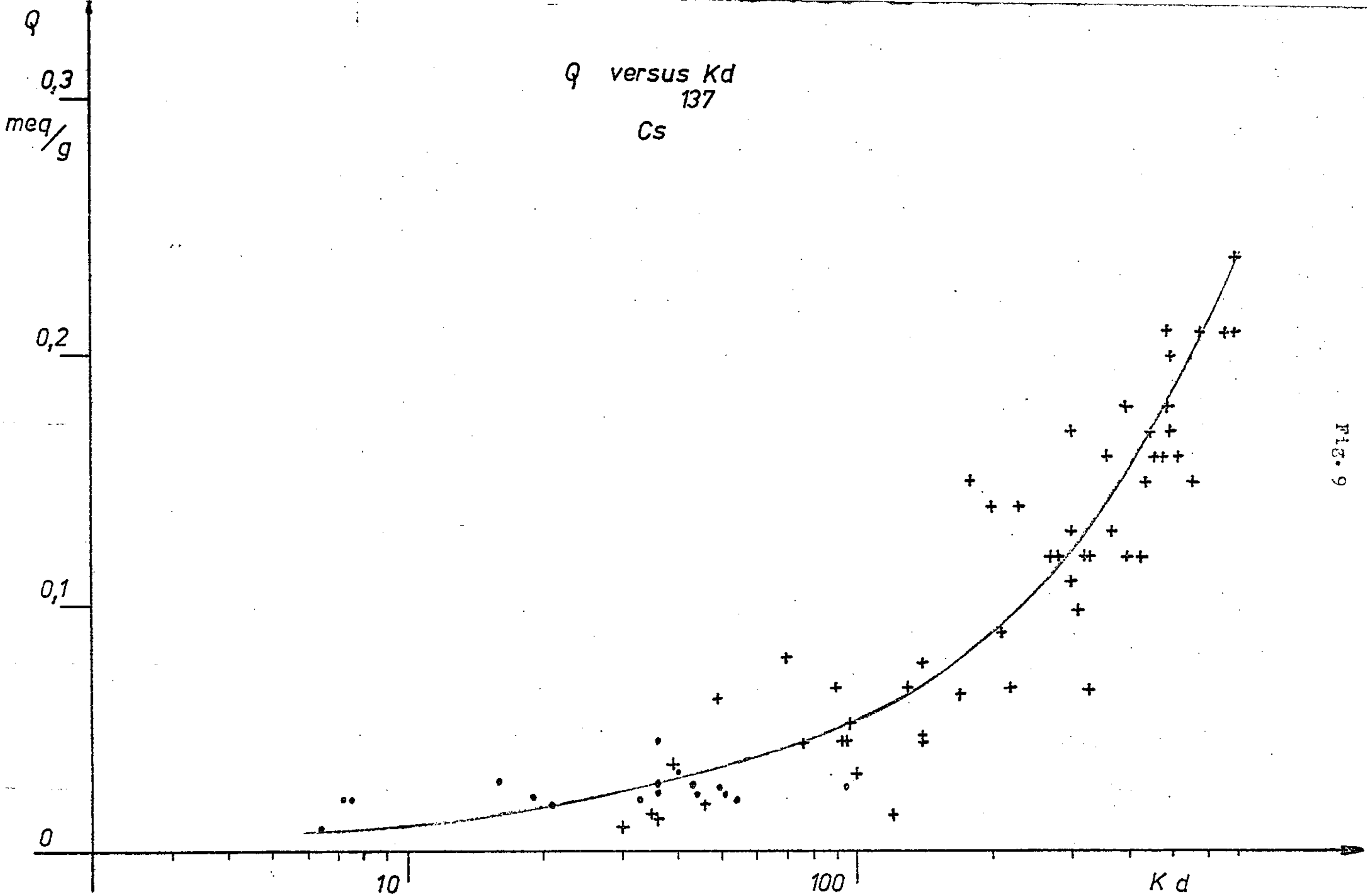


Fig. 9

Fig. 10

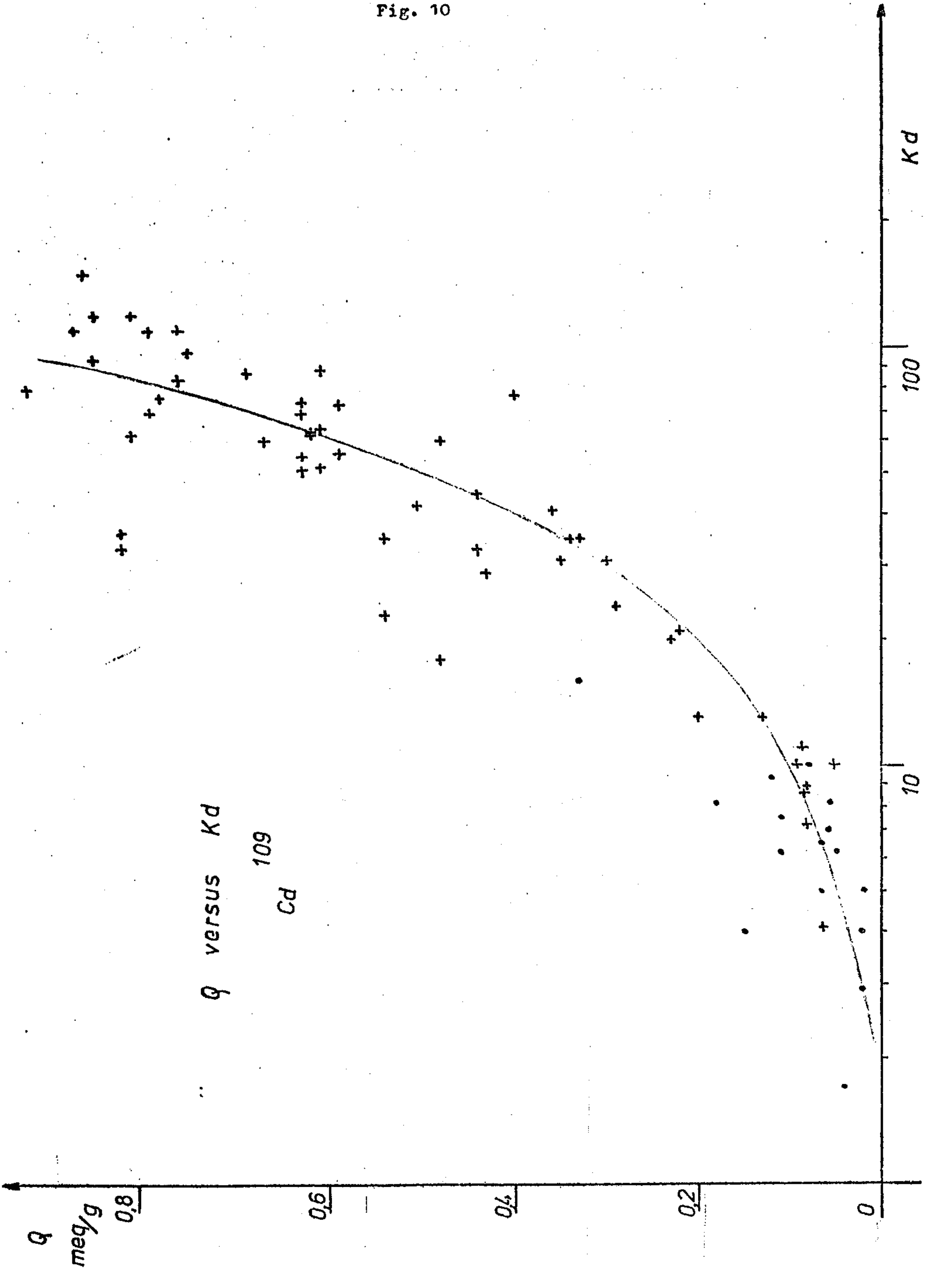


Fig.11

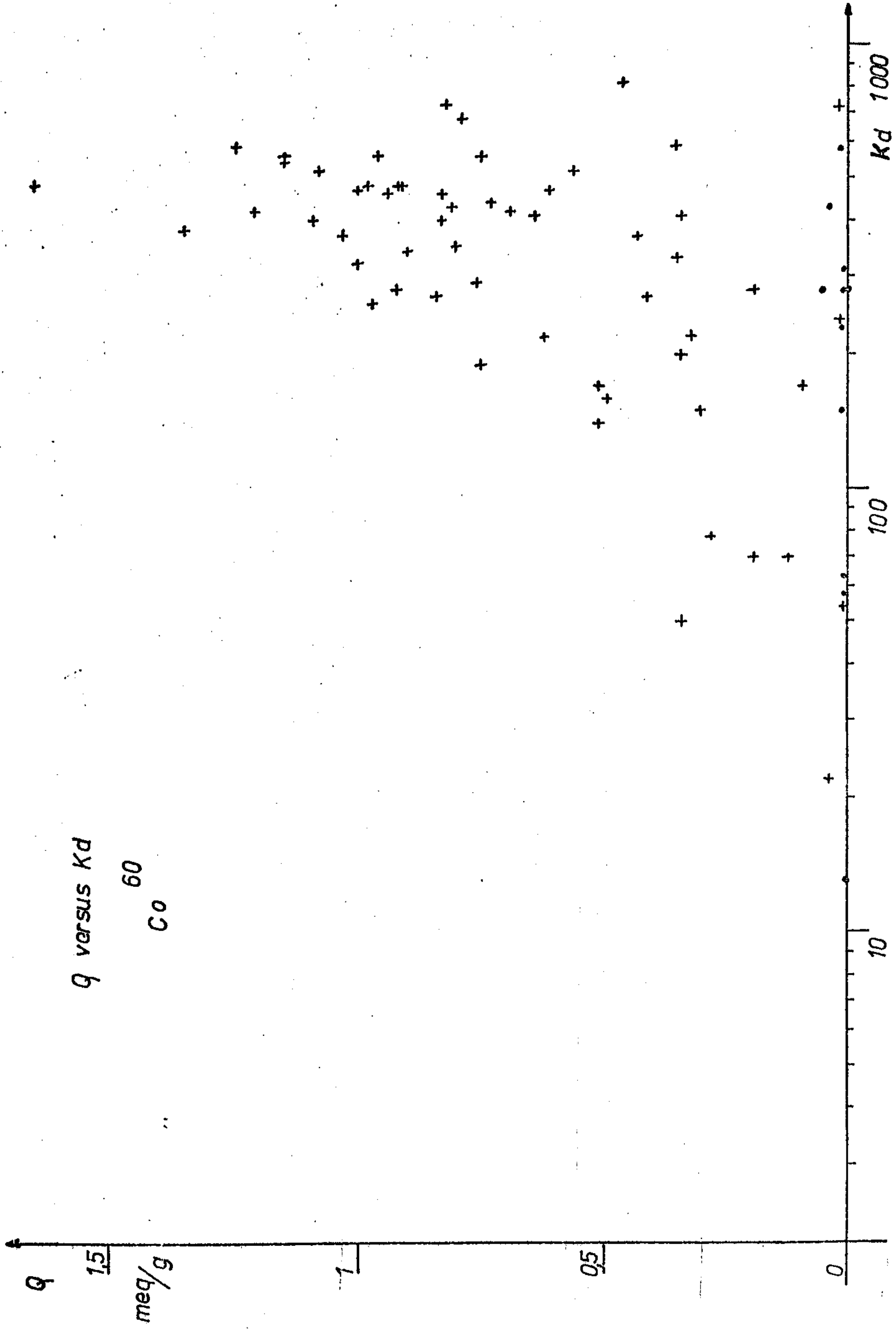


Fig. 12

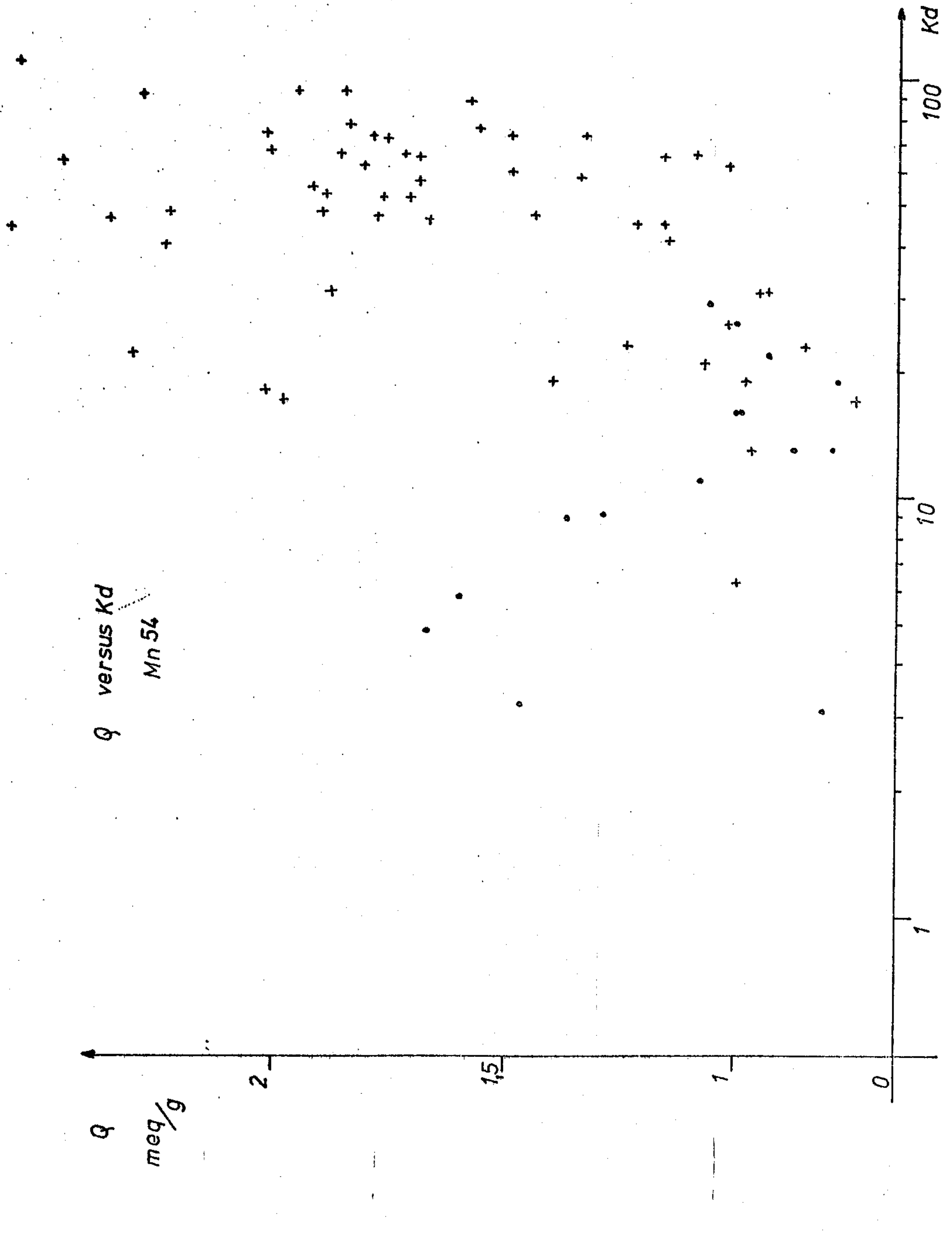
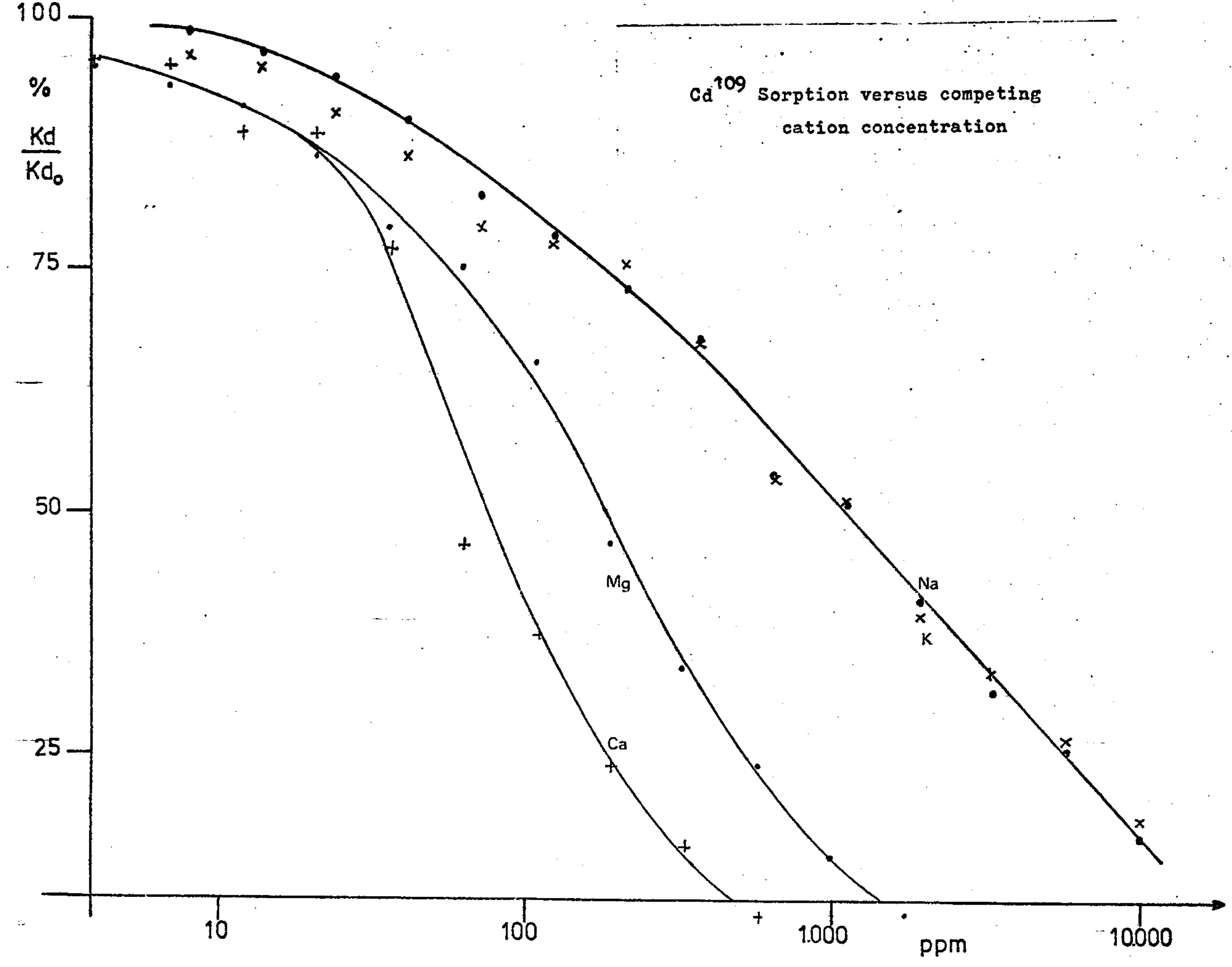
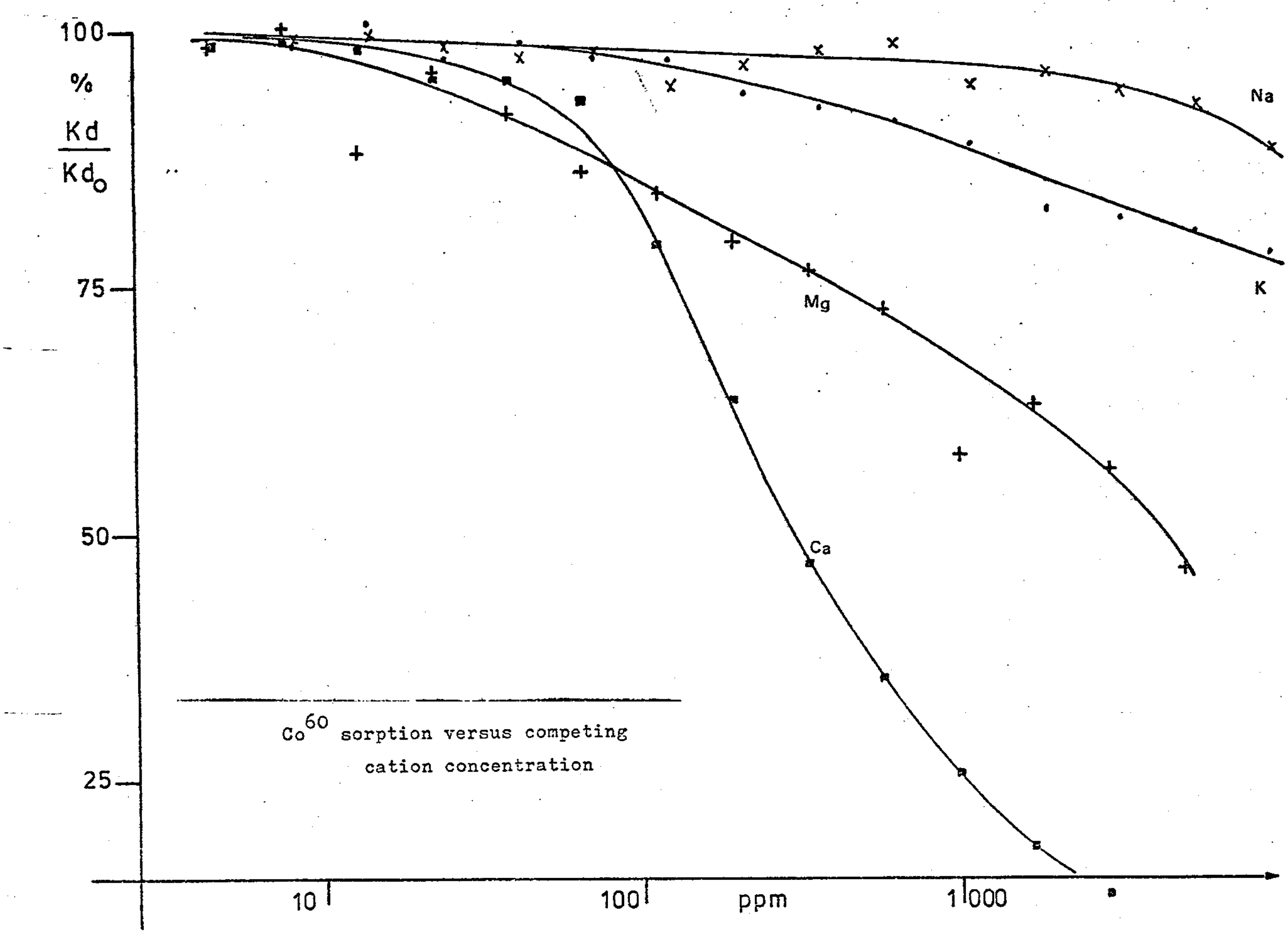


Fig. 13



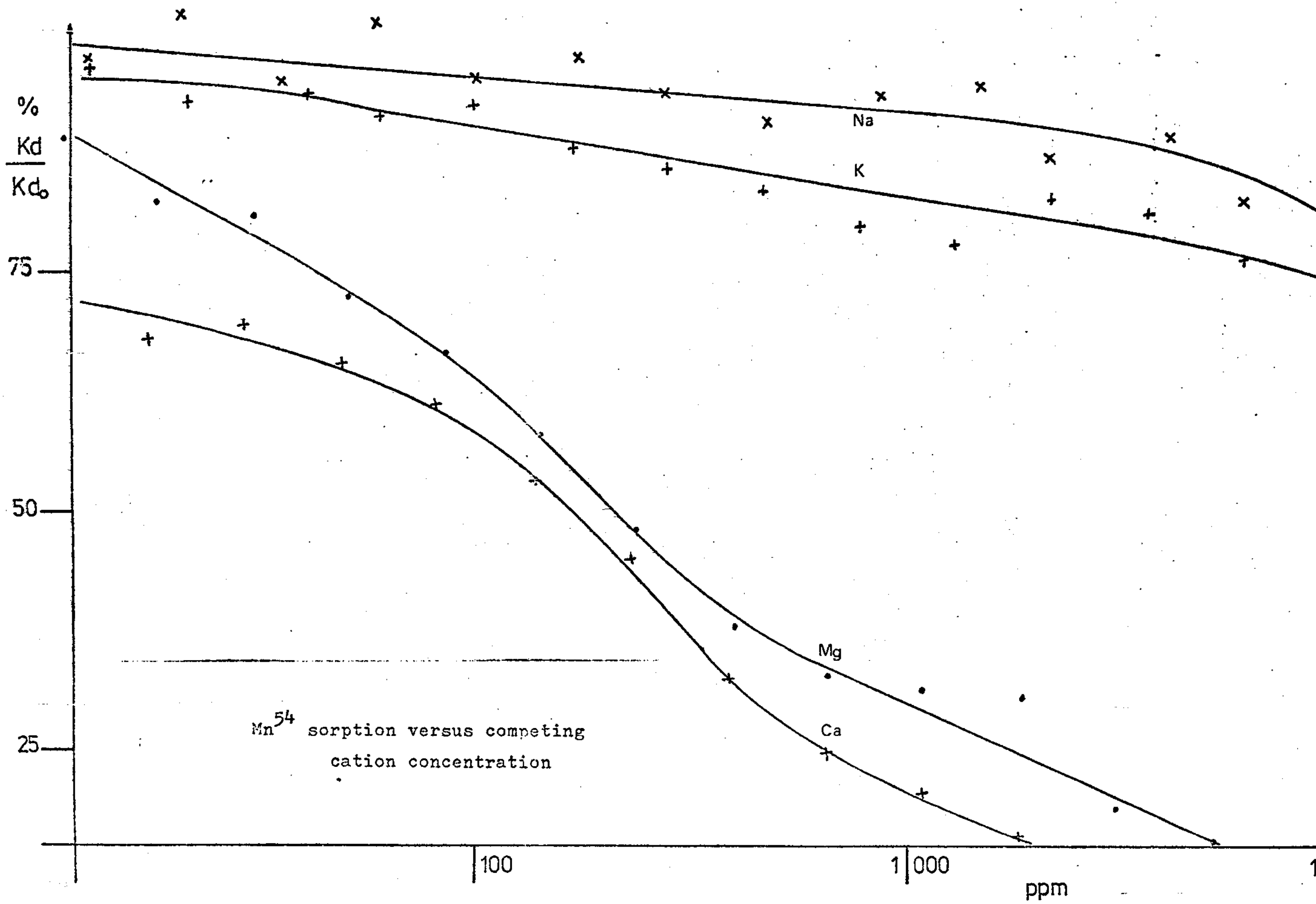
Cd^{109} Sorption versus competing cation concentration

Fig. 14



Co^{60} sorption versus competing cation concentration

Fig. 15



Mn^{54} sorption versus competing cation concentration

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 Mn^{54}, Co^{60} and Cd^{109} this influence is much smaller than with Cs^{137} 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.

Cd^{109} sorption versus Cd concentration

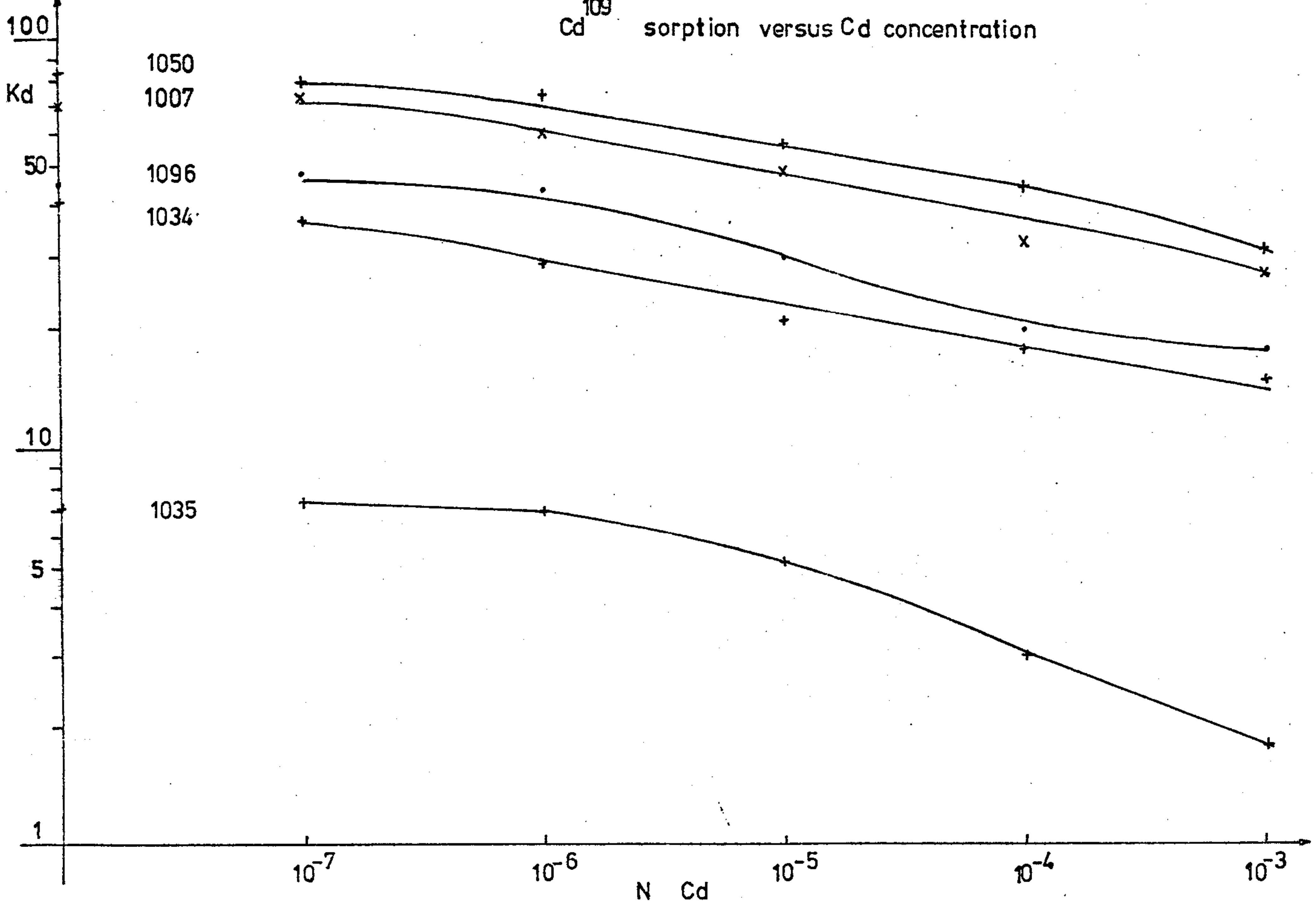


Fig.16

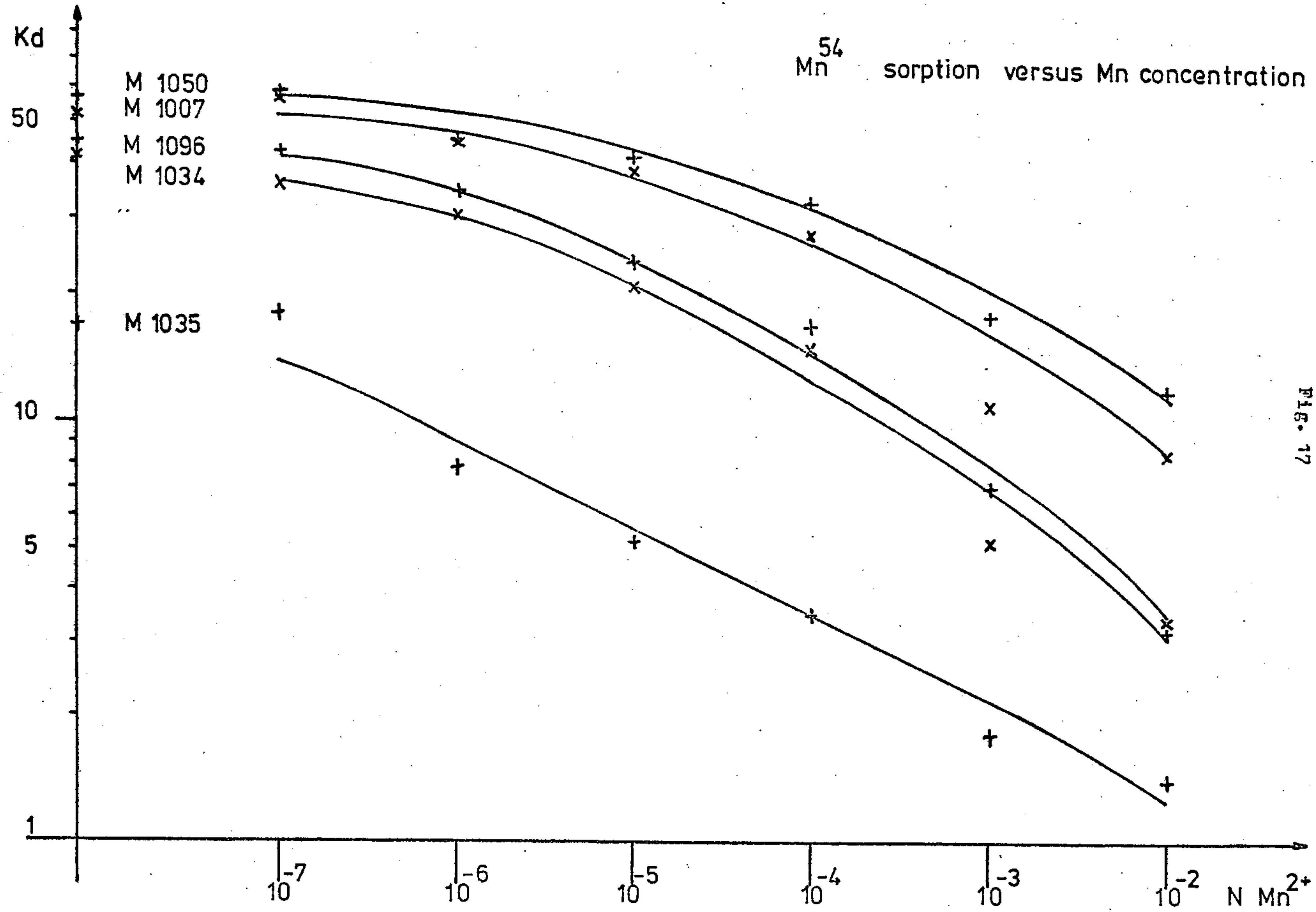
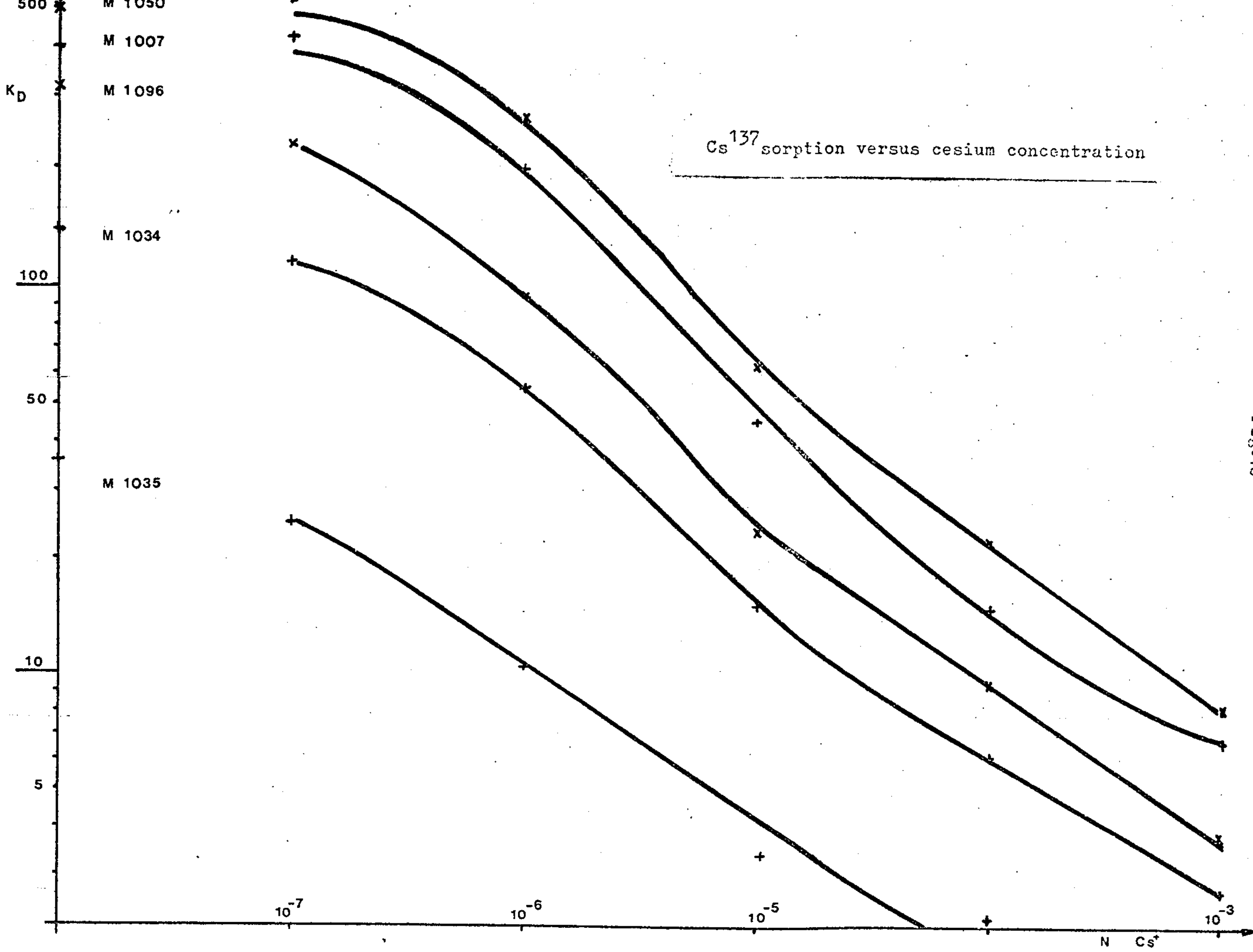

Kd
50
10
5
1
M 1050
M 1007
M 1096
M 1034
M 1035
^{54}Mn sorption versus Mn concentration
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
N Mn^{2+}

Fig. 17

Fig.18


Cs^{137} sorption versus cesium concentration
K_D
500
100
50
10
5
M 1050
M 1007
M 1096
M 1034
M 1035
10^{-7}
10^{-6}
10^{-5}
10^{-3}
N Cs^{+}

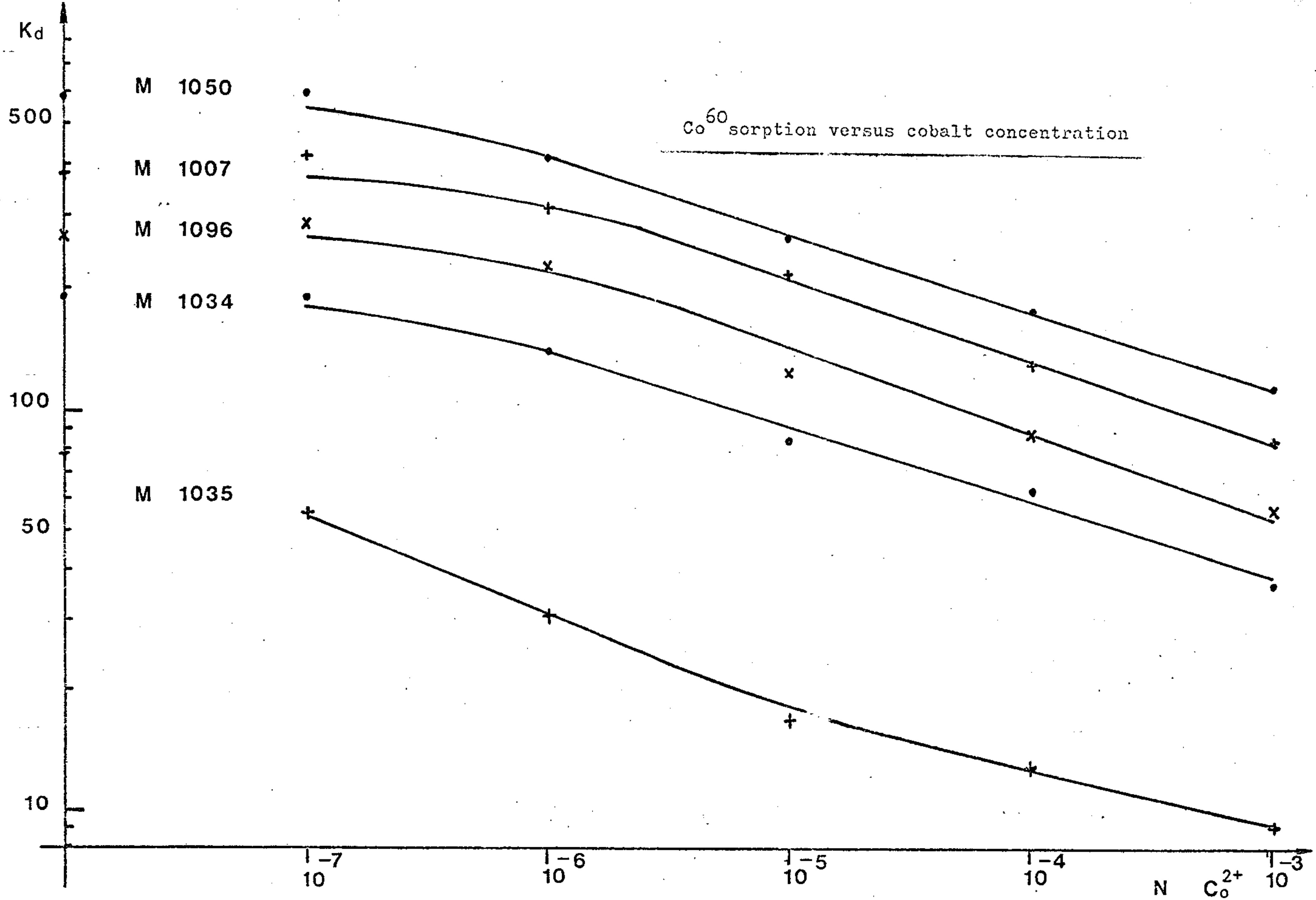

Co^{60} sorption versus cobalt concentration
K_d
500
100
50
10
M 1050
M 1007
M 1096
M 1034
M 1035
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
N C_o^{2+}

Fig. 19