

C.I.P.S.

MODELE MATHEMATIQUE DE LA  
POLLUTION EN MER DU NORD.

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Sorption by some North Sea Sediments

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The purpose of this report consists in gathering data on the sorption of specific radioisotopes on natural bed sediments of the Scheldt and the North Sea. Especially the sorption capacity (Q) of the sediments and the distribution coefficients (Kd) of specific ions will be used. The expression of sorption will be understood here as any reaction between the sediment and the radioactive solution, which will consequently cover both absorption and adsorption reactions. The quantity of a specific radioactive substance that can be accepted by suspended particles or by bottom-sediments does not depend exclusively on the physical and chemical properties of the ion and of the sediment, but also on a number of environmental factors. For radionuclides in cation shape, which occur most often, the sorption by sediments and the exchange balances between sediment and water are of great importance.

About hundred bottom samples of the thousand points system were examined. Their characteristic sorption features with regard to cesium, cobalt, cadmium, strontium, manganese and zinc were investigated. The following values have been determined: the sorption capacity with respect to a 1 N solution and the distribution coefficients in seawater with respect to the same ions in tracer quantities. For these determinations we always used radioactive tracers i.e. Cs<sup>137</sup>, Cs<sup>134</sup>, Co<sup>60</sup>, Cd<sup>109</sup>, Mn<sup>54</sup>, Sr<sup>85</sup> and Zn<sup>65</sup>.

Figure 1 shows the specimens examined and their place within the thousand points system. Most specimens are from locations quite close to the coast for the reason that we wished to begin by examining above all clay and silt specimens since their sorption features are much more pronounced as compared to those of sand-containing specimens. Currently we are also investigating sand-containing specimens in order to get a better picture of changes in characteristic features over the entire area examined.



#### Processing of sediments.

The samples are dried for minimum one week, at a maximum temperature of 50° C. Then they are finely ground in a mortar. For part of the sample is achieved a fractionation of < 150  $\mu$  by means of dry sifting, and a fractionation of < 300  $\mu$  for another part. Both fractions are examined when determining capacity and distribution coefficients. The sea water is filtered immediately upon arrival and again just before used for the tests.

#### Sediments capacity determinations.

The capacity indicates the sediments potential sorption properties. Concentrations of 1 N are used for capacity determinations.

Approximately 0.2 g of sediment is weighed in a test tube. Excess ions present are eliminated by rinsing with demineralized water. For this purpose is added  $\pm$  5 ml of water, the test tube is thoroughly shaken during approximately ten minutes and then centrifuged. Pour off the clear supernatant liquid. This is repeated until the rinsing water is free of chloride. Now is added the CsCl solution (5 ml 1 N) previously marked with Cs<sup>137</sup>. After thorough mixing, the test tube is shaken during minimum four hours. Then centrifuge and pour off the supernatant liquid. This is repeated another two times. Take care that minimum twenty times the sample's capacity is present in the solution. Excess CsCl in the sample is rinsed off with 10 ml shares of 95 % ethanol. Shake and centrifuge until the discarded ethanol is free of chloride. Wash outer edge of the test tube with dilute HCl and rinse in demineralized water.

After drying, the test tube is analysed in a NaI(Tl)-scintillation counter with well crystal. The initial solution, too, is measured in the same crystal and with the same metering arrangement.

Capacity is expressed in milliequivalents per gram:

$$Q = \frac{\text{sample : counts per minute and per gram}}{\text{solution : counts per minute and per meq.}}$$

Figures 2,3,4,5 and 6 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 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 meq/g), with Sr < 0.5, they remain for all samples with Mn > 0.6 meq/g.





North Sea bottom samples

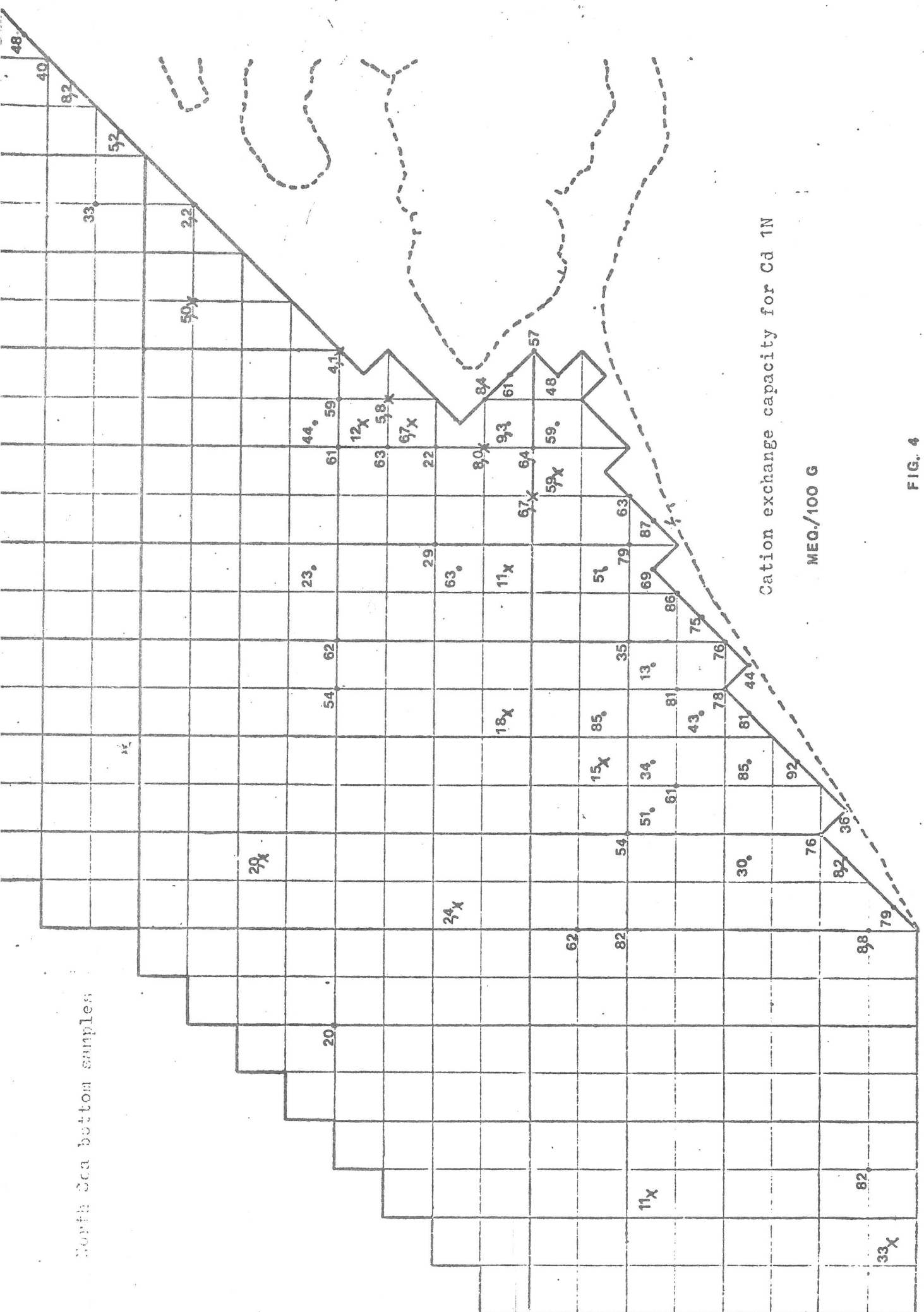
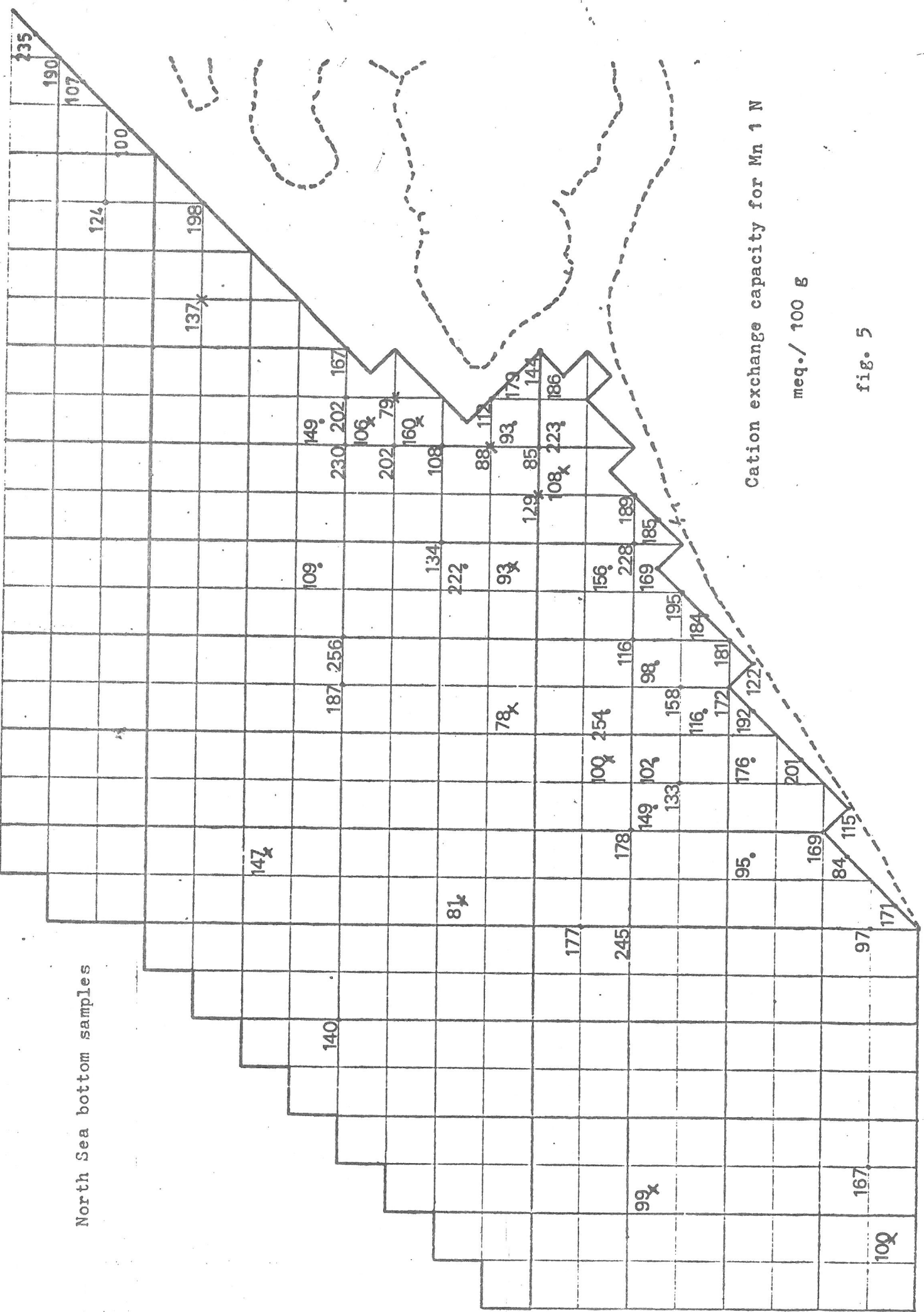


FIG. 4



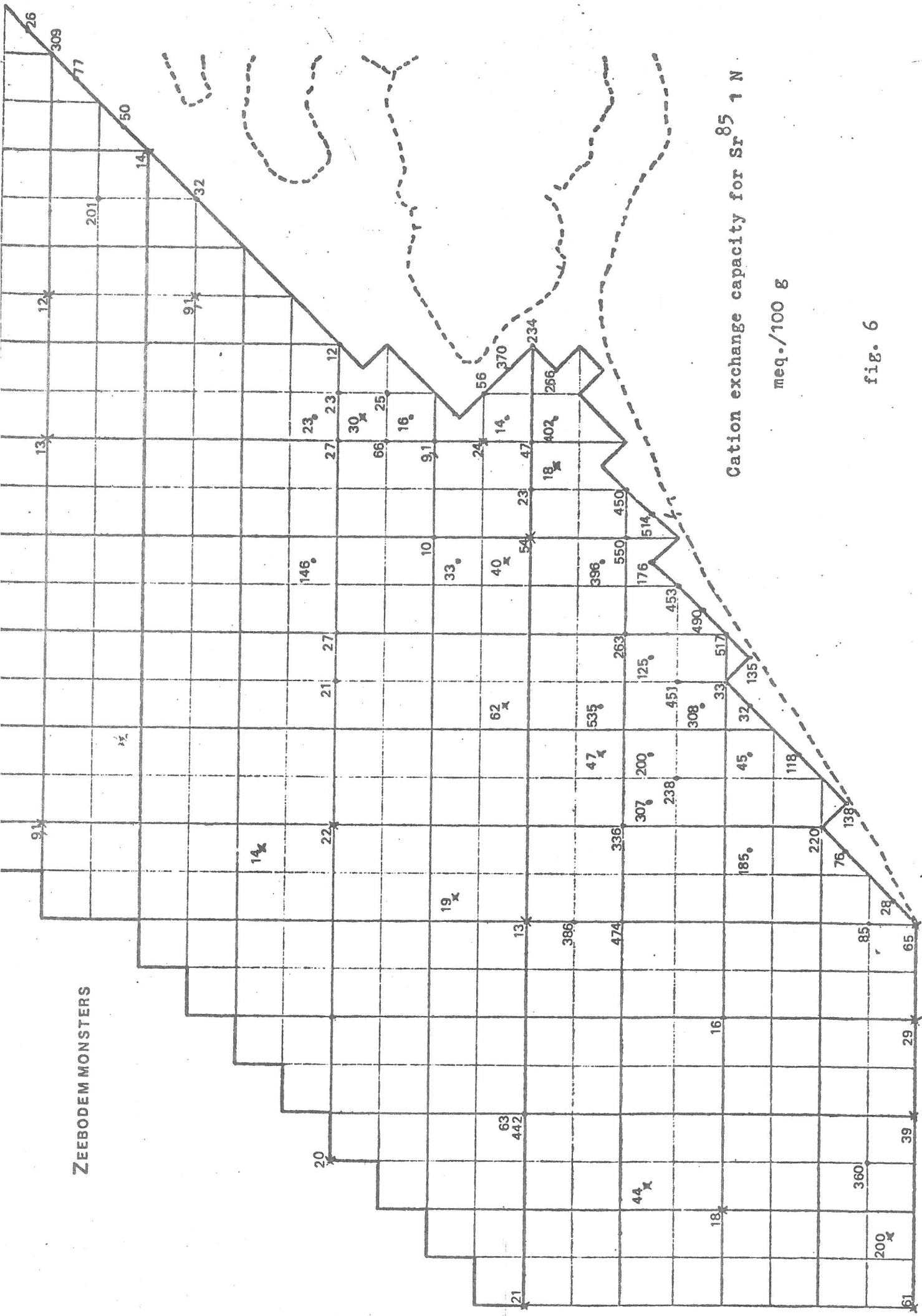
North Sea bottom samples



Cation exchange capacity for Mn 1 N  
meq./ 100 g

fig. 5

ZEEBODEM MONSTERS



Cation exchange capacity for Sr<sup>85</sup> 1 N  
meq./100 g

fig. 6

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 ( 1 M solution ! ) from the sediment.

Determination of distribution coefficient ( Kd ).

The distribution coefficient shows the ratio at equilibrium of the concentration in the solid phase and that in the fluid phase.

$$Kd = \frac{\text{Conc. in sediment}}{\text{conc. in solution}} = \frac{C_o - C_e}{C_e}$$

$C_e$  = Equilibrium concentration in the solution

$C_o$  = Concentration at the beginning in the solution

For the exchange of monovalent cations we may write:



The equilibrium constant will then be:

$$K_M^{Cs} = \frac{[\text{M}^+] [\text{Cs-sed.}]}{[\text{M-sed.}] [\text{Cs}^+]} = \frac{Kd_{Cs}}{Kd_M}$$

In sea water and river water, various other types of ions will be present in excess and their concentrations at the sediments exchange locations are generally unknown. For radionuclides in tracer quantities, however, the fraction of exchangeable locations they occupy will be extremely small. Consequently, we may consider, in the comparison here-above  $[M^+]$  and  $[M\text{-sed.}]$  as constants and we may write:

$$K_M^{137Cs} = \frac{[Cs\text{-sed.}]}{[Cs^+]} = Kd_{Cs}$$

And this only if cesium is present in tracer quantities. In this case, the distribution coefficient will describe the equilibrium. This, however, will apply only for this specific sediment in water with this specific composition.

Process method:

A fixed quantity ( 0.1 g ) of the sediment is shaken with 20 ml of sea water with added tracer. For this we use small containers of 25 ml . After a certain time of shaking, the solution is centrifuged or left to settle for an entire night. Part of the supernatant liquid ( 1-2 ml ) is pipetted off and measured. This is repeated until the value of the Kd remains constant, it may generally expected to occur after about seven days.

$$K_d = \left( \frac{\text{initial activity in the solution}}{\text{final activity in the solution}} - 1 \right) \times \left( \frac{V}{S} \right)$$

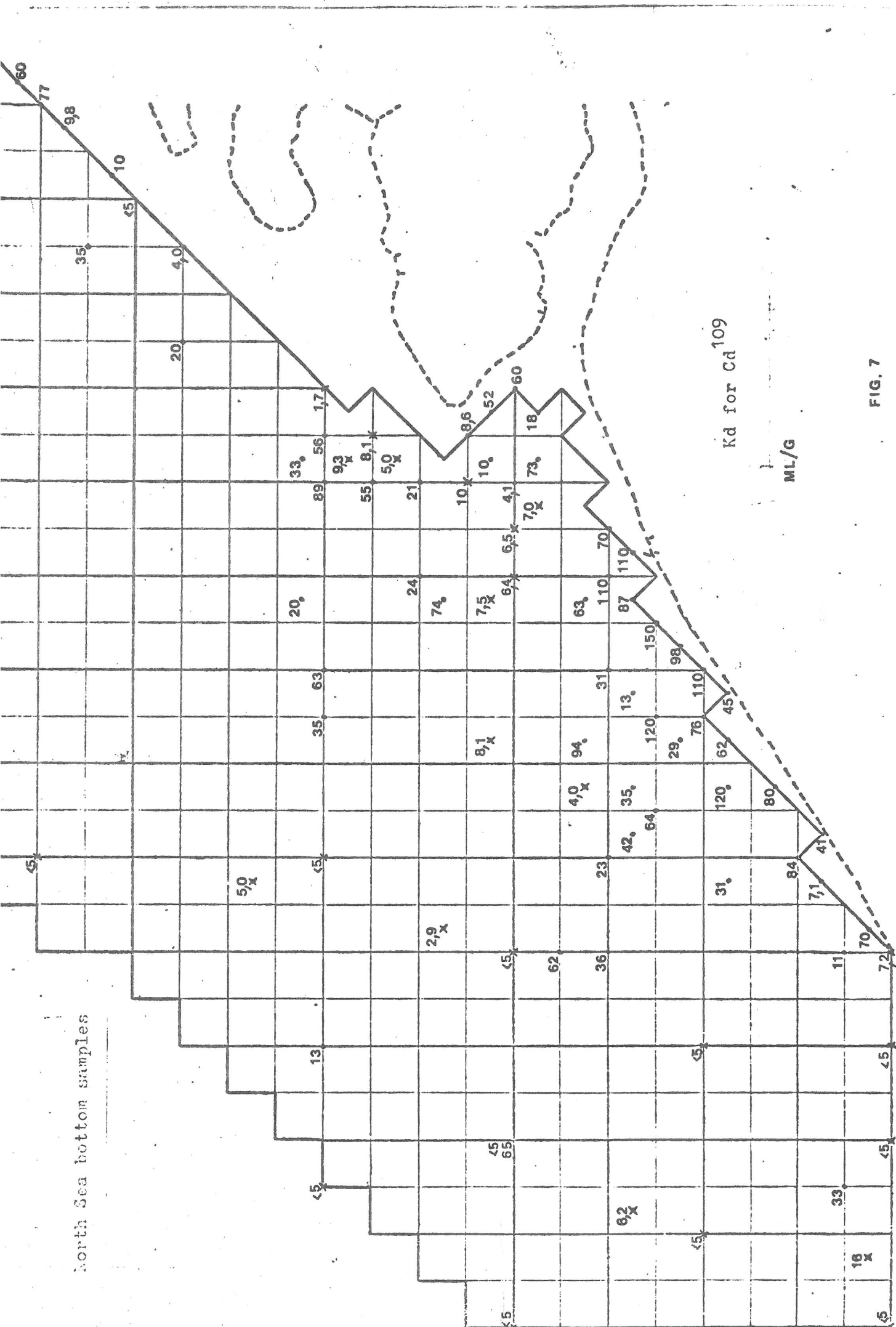
Figures 7, 8, 9, 10 and 11 show distributions coefficients (  $K_d$  ). These present a truer picture of what may occur in seawater upon contact with sediments. They were determined in seawater and, with respect to the element, in tracer quantities. Distribution coefficients as determined show the following picture for the various radioisotopes:

$$\text{Zn} \gg \text{Co} \geq \text{Cs} \gg \text{Mn} \approx \text{Cd} \gg \text{Sr}$$

The  $K_d$  is always less than 10 for Sr. With all others, we determined small  $K_d$  values for definitely sandy samples (  $K_d < 50$  for Co, Cs, Mn and Cd;  $K_d < 300$  for Zn ) while for samples rich in clay or in silt, such values rise to 100 with Mn and Cd, to 600 with Co and Cs and to 5,000 with Zn. Considering the number of specimens examined and the considerable differences where soil structure is concerned, it will still be impossible, however, to define areas on the maps. This explains why the maps show only the value determined at that specific point.

Another method used for  $K_d$  determination was the sedimentation method ( Duursma 1970 ). Tests conducted in this manner always supplied smaller  $K_d$  values as compared to those obtained by shaking. The reason for this is probably an overly quick sedimentation resulting in deficient balance. Although this determination method may be most appropriate for following some processes in nature, it was nevertheless abandoned because the results obtained featured excessive

North Sea bottom samples

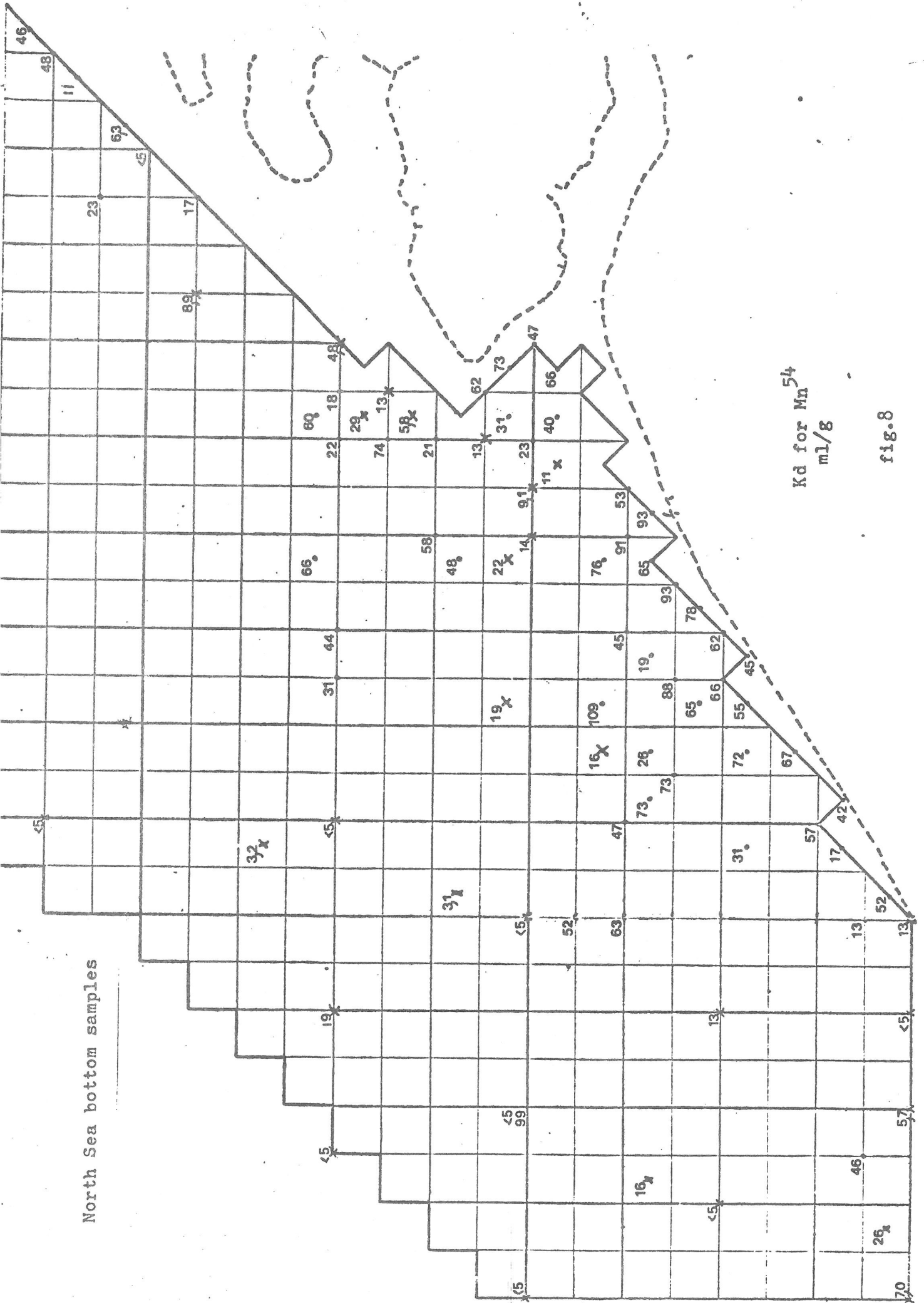


Kd for Cd<sup>109</sup>

ML/G

FIG. 7

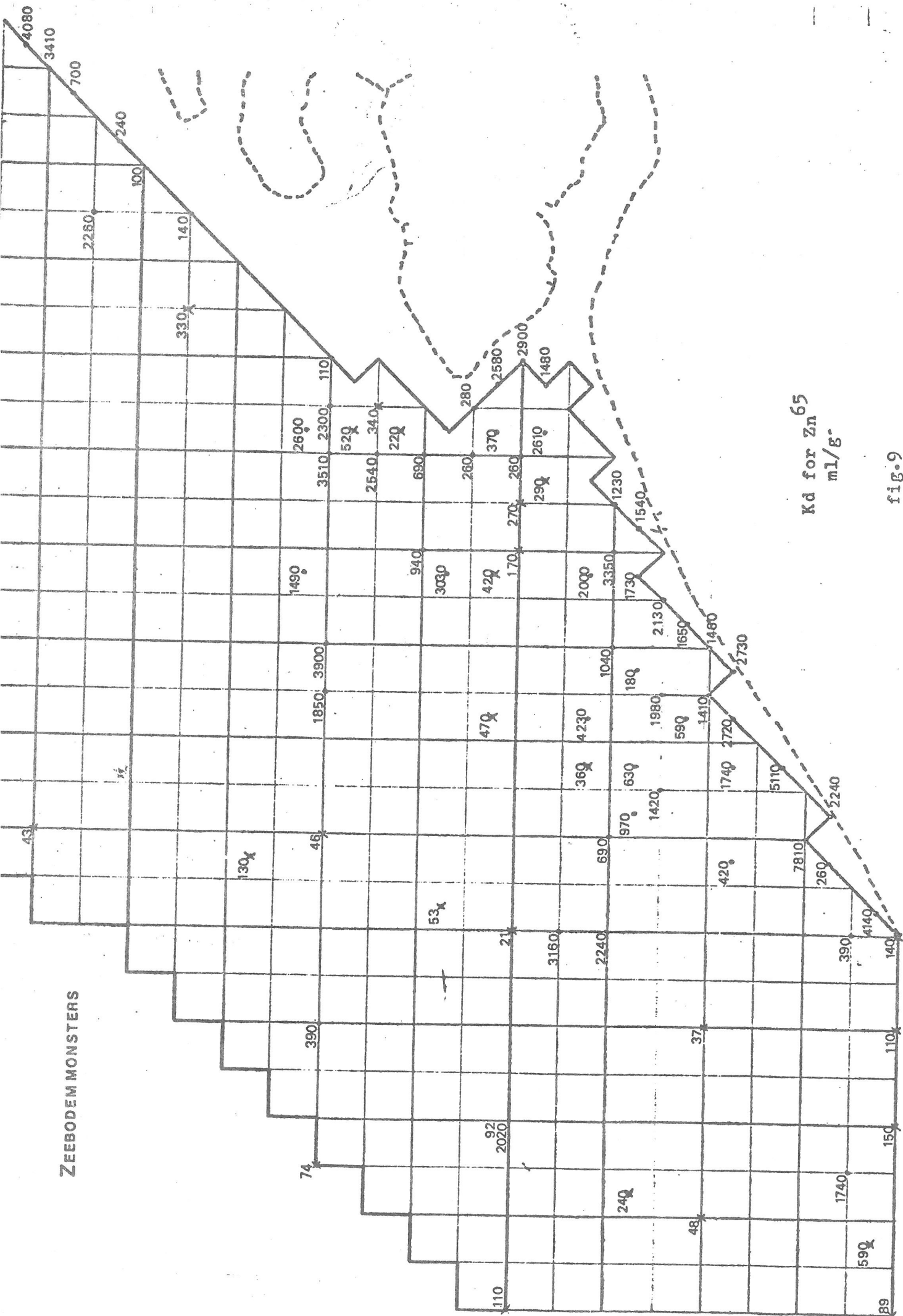
North Sea bottom samples



Kd for Mn<sup>54</sup>  
ml/g

fig.8

ZEEBODEM MONSTERS



Kd for Zn<sup>65</sup>  
ml/g.

fig.9







spreading produced by the influence of grain size, sedimentation height and sediment input system.

When comparing values measured with regard to capacity and  $K_d$  for one and the same ion, we note a definite connection to be established between the two quantities only with Cs and Cd (fig. 12, 13). With Co and Mn there appears to be no actual connection (fig. 14, 15). Investigations conducted by Duursma on soil samples from all over the world have produced the same results where Cs is concerned. They also establish a connection with Zn. Duursma did not investigate Cd. We also found a certain correlation to exist between capacity and  $K_d$  as determined with Cd and Cs for one and the same sample. Duursma did not determine any connection, either, between  $K_d$  and  $Q$  with Co and Mn. For this reason and supported by sorption reaction speed determinations, he draws the conclusion that there can be any exchange of ions only with Cs and Zn while various mechanisms play a more important part regarding the other radioisotopes (precipitation, isotopic exchange, complex formation .....).

Fig. 12

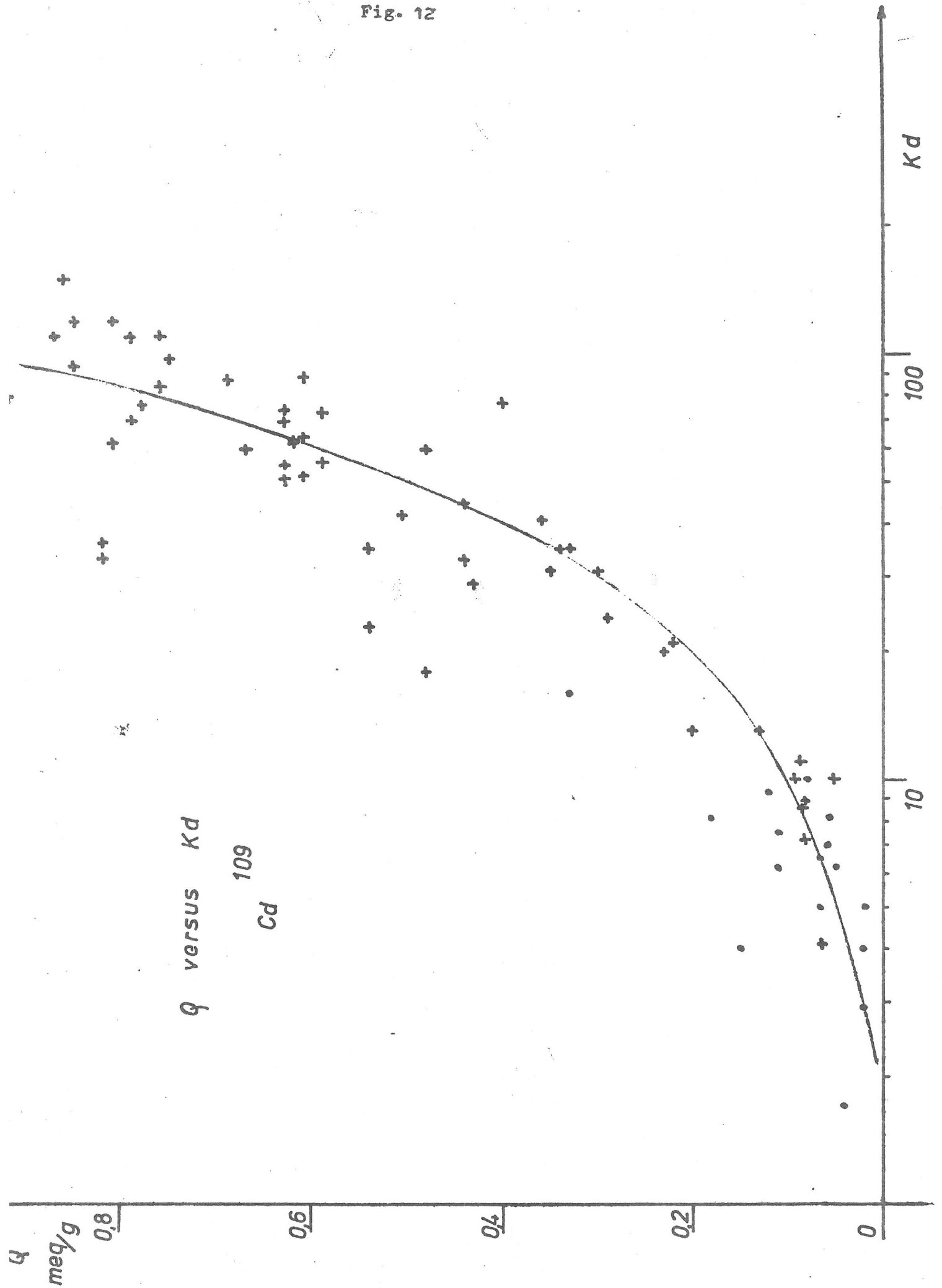


Fig. 13

Q versus  $K_d$   
 $^{137}\text{Cs}$   
req/g

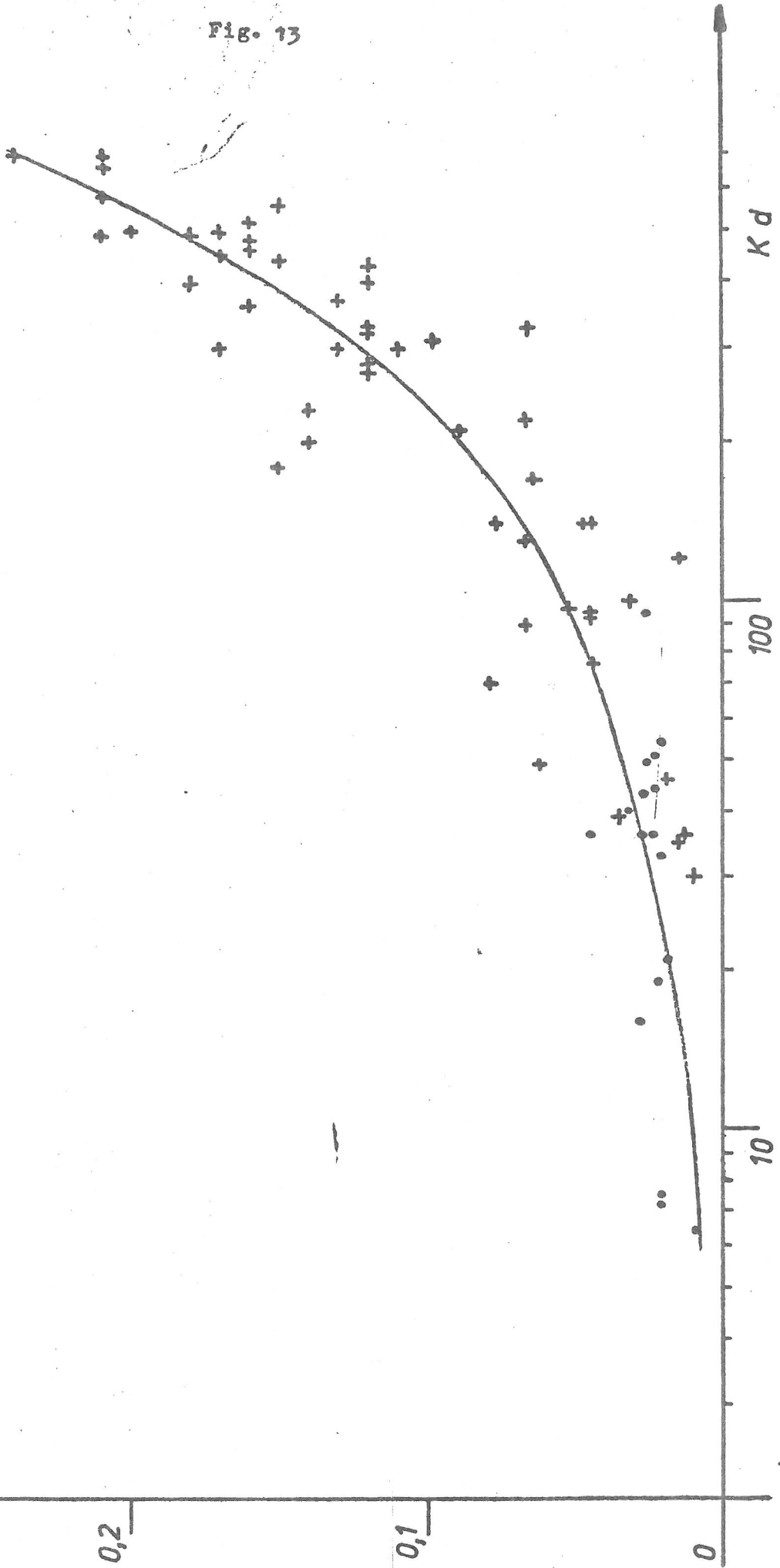


Fig. 14

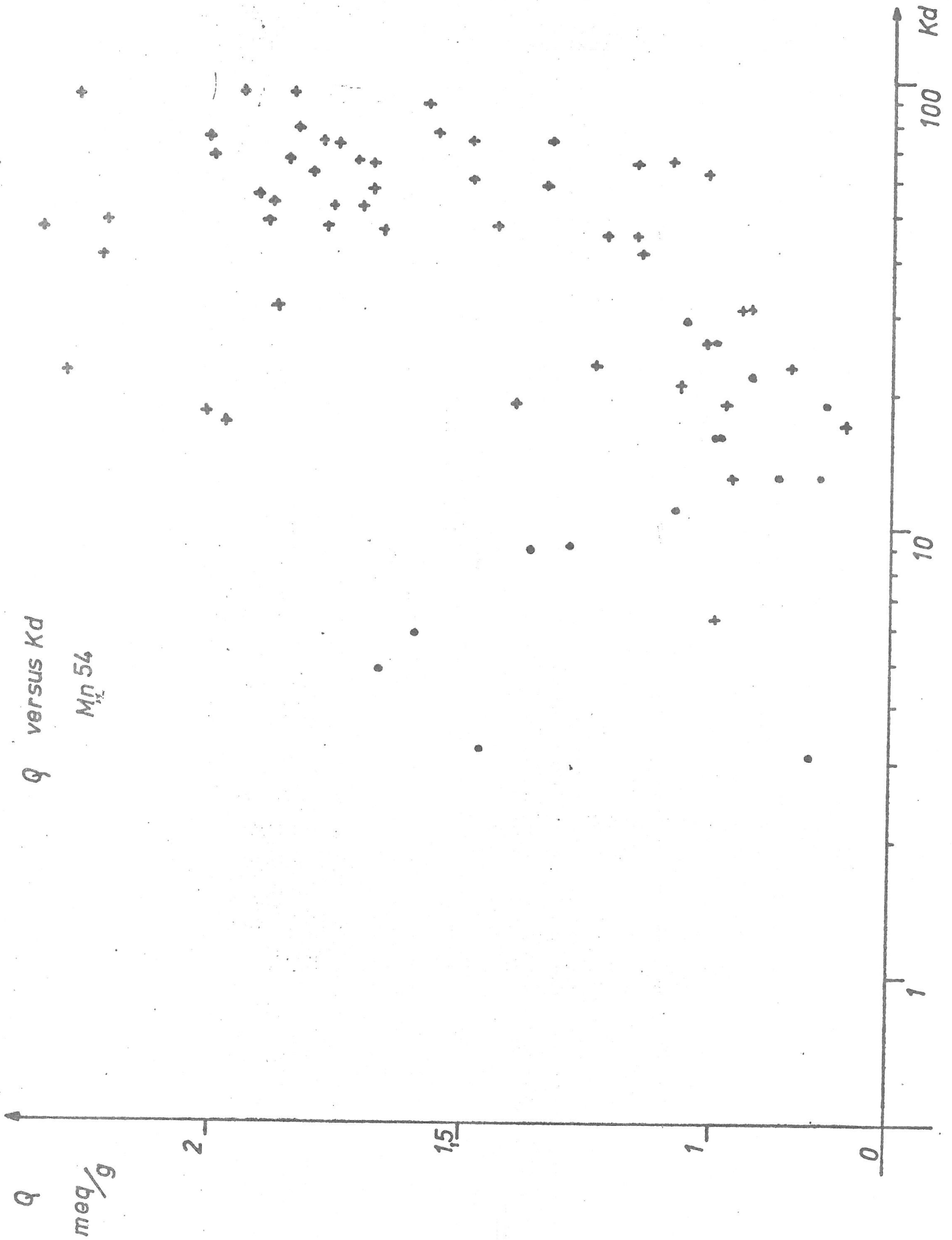
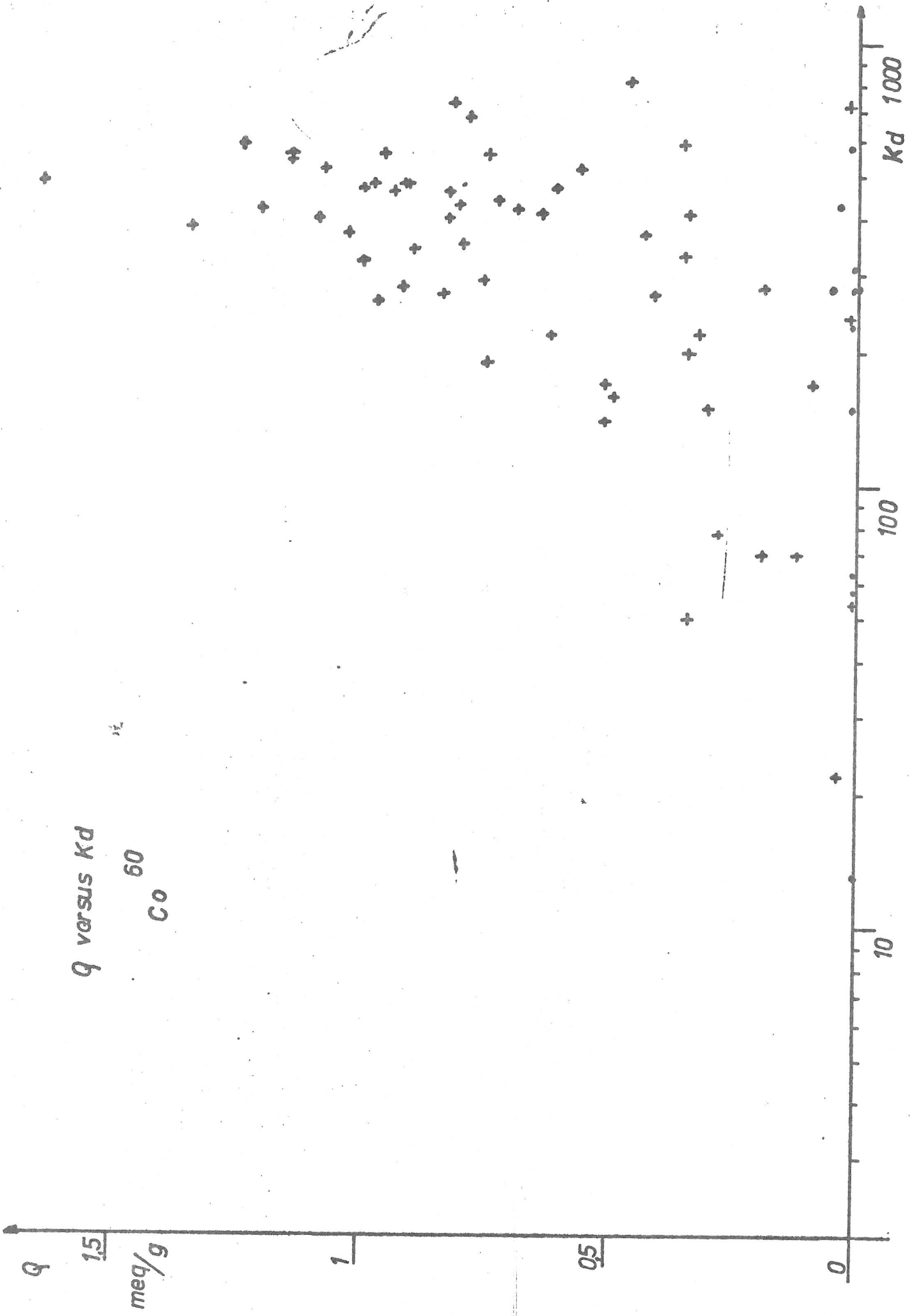


Fig. 75



The influence exercised by other ions ( Na, K, Ca and Mg ) on the sorption of Cs, Co, Cd, Mn and Zn was also investigated. While with Cs, it was mostly Na and K which caused significant decrease of Kd whereas Ca and Mg exercised a lesser influence, conditions were different where bivalent radioisotopes are concerned. With Cd<sup>109</sup> and Sr<sup>85</sup>, the differences between monovalent and bivalent ions were considerably less pronounced. Ca and Mg exercised a greater influence here as compared to Na and K . We obtained the same picture again with Mn<sup>54</sup> and Co<sup>60</sup> sorption where the influence exercised by Na and K decreased considerably (fig. 16, 17, 18, 19, 20 and 21 ).

With Zn<sup>65</sup> we obtained a very different response. The value of Kd was only slightly dependent on Na and K concentration and featured a rising tendency with higher concentrations of these ions. For Ca we obtained first rising Kd values and, subsequent to a maximum value, the conventional curve response where the influence exercised by Ca on the sorption of Zn increased heavily again. Other processes than ion exchange probably have a part to play in this context.

Tests were conducted with Hg<sup>203</sup>. Because the major part of activity was lost at the walls of the jars, conditions prevented these test from being carried out. The seawater pH was probably too high to permit working with Hg<sup>2+</sup> ions. Consequently, the tests in seawater could not be performed.



fig. 16

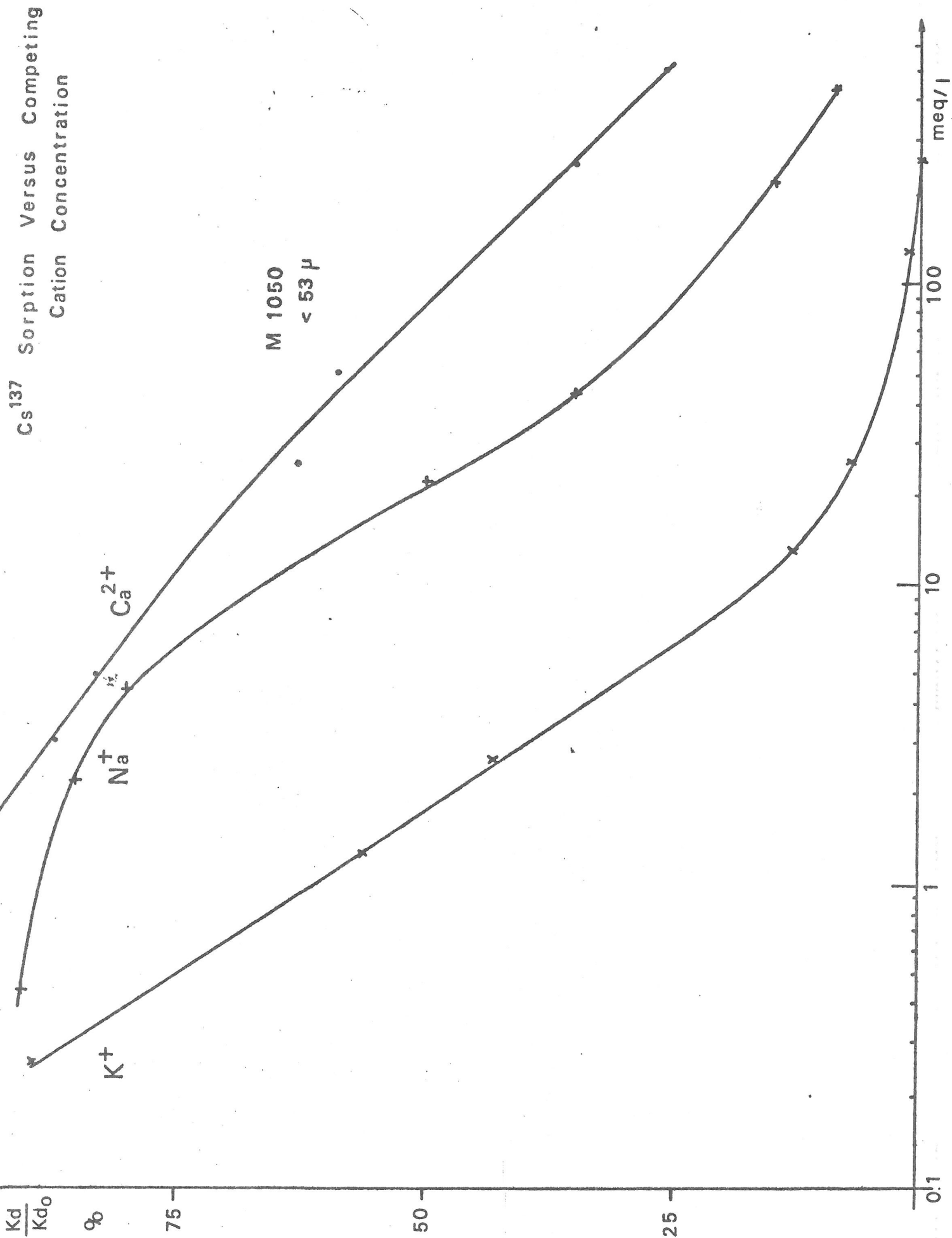
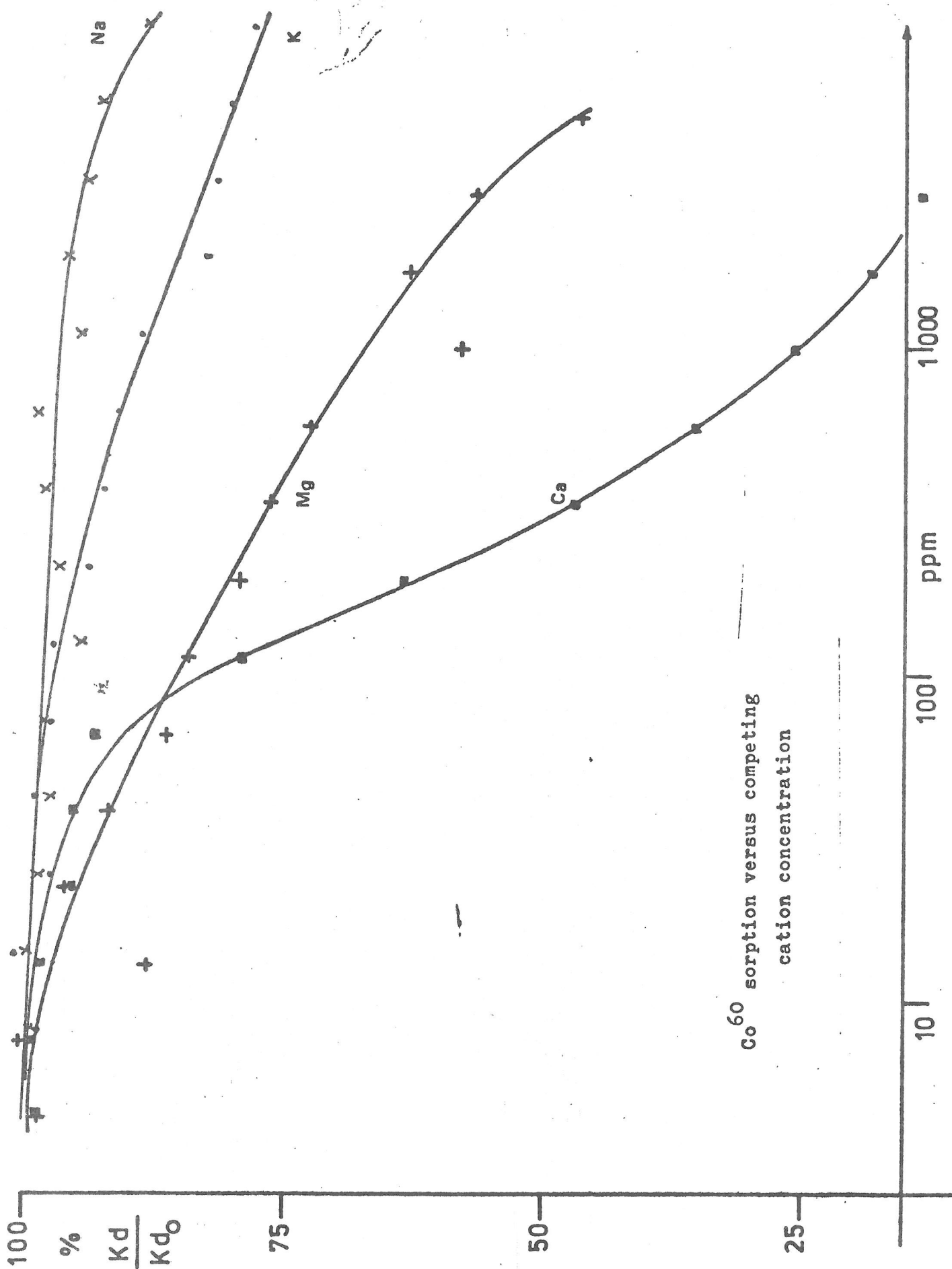


Fig. 17



$Co^{60}$  sorption versus competing  
cation concentration

Fig.18

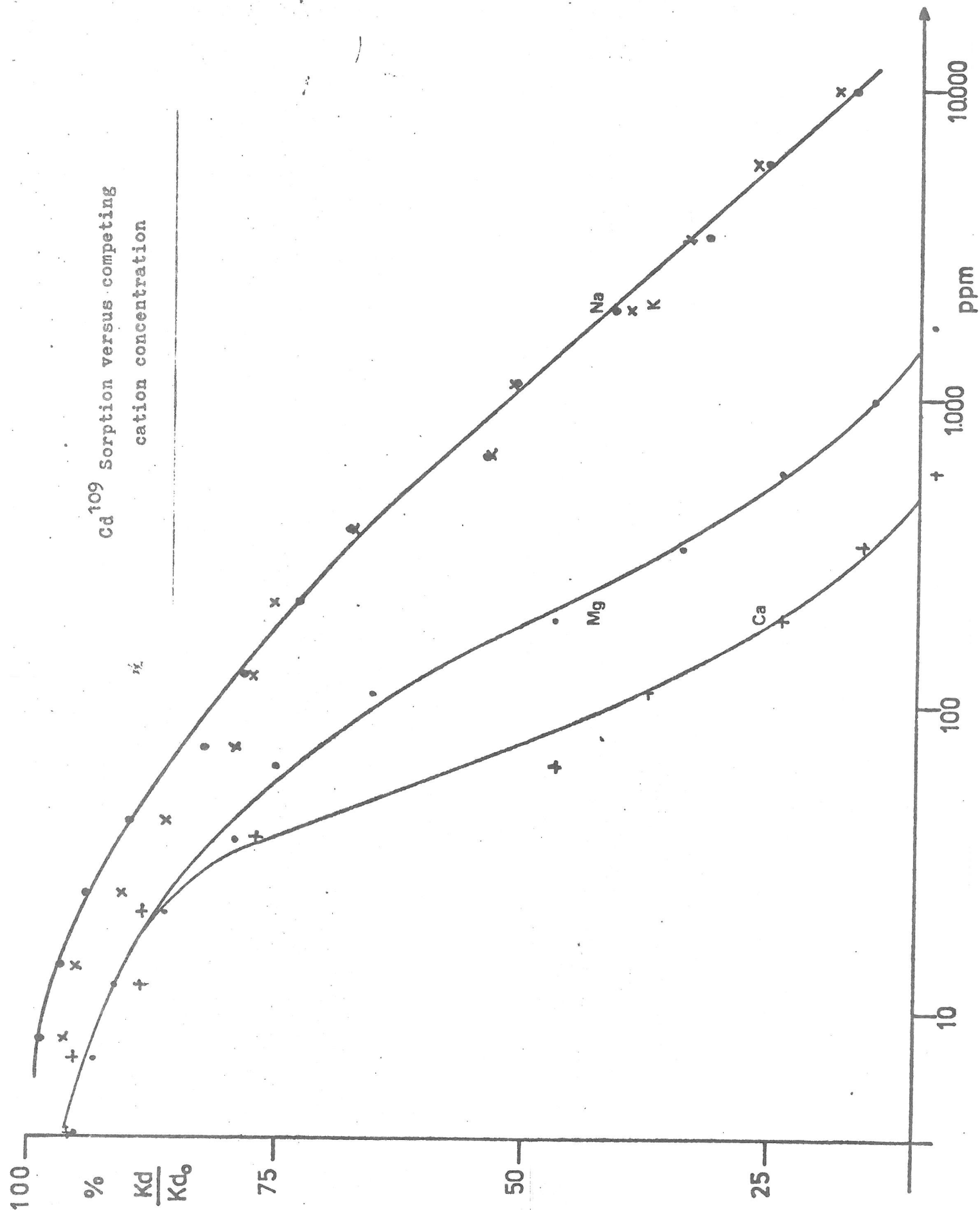
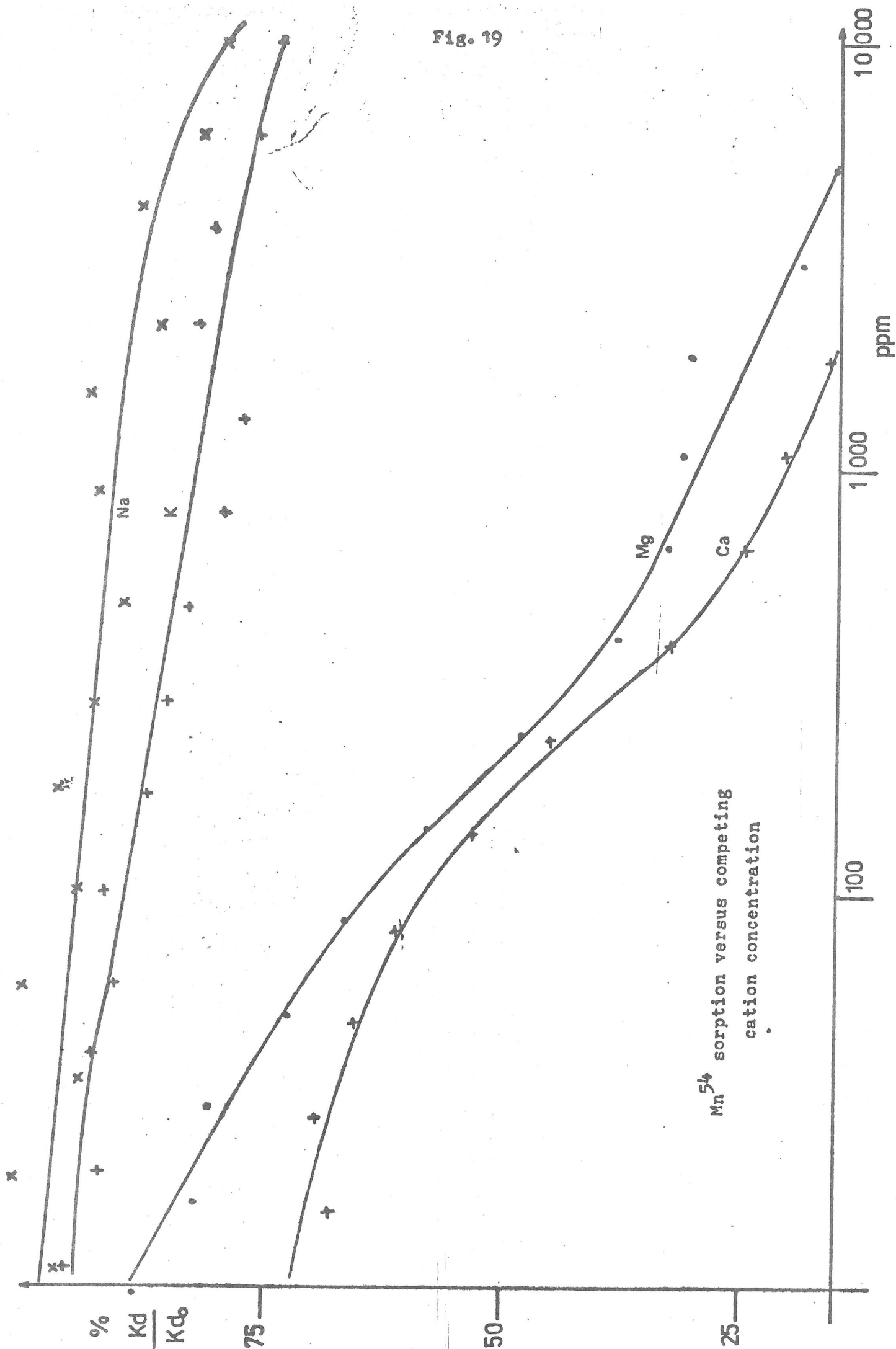


Fig. 19



$Mn^{54}$  sorption versus competing cation concentration

fig. 20

$Sr^{85}$  sorption versus competing  
cation concentration

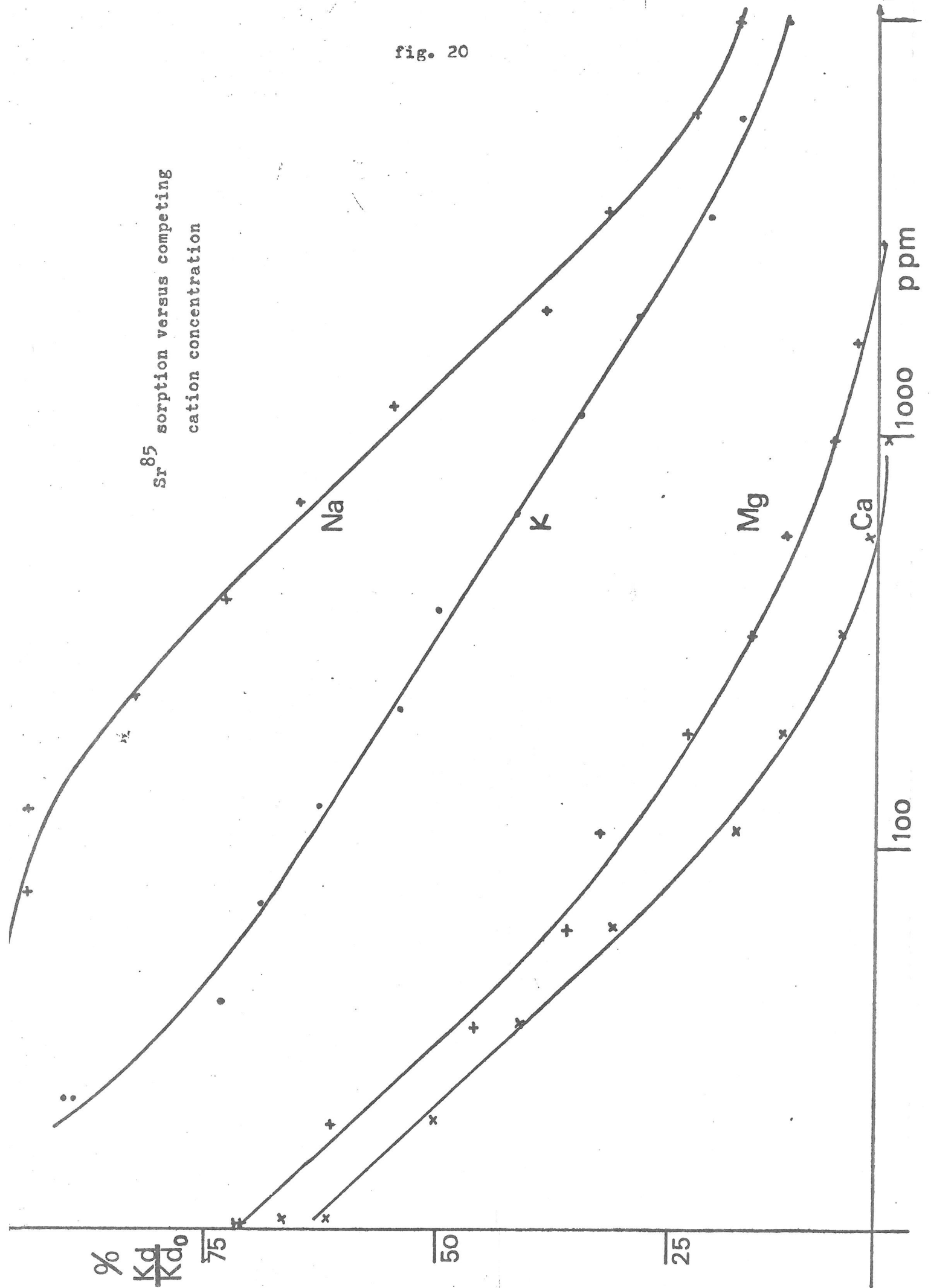
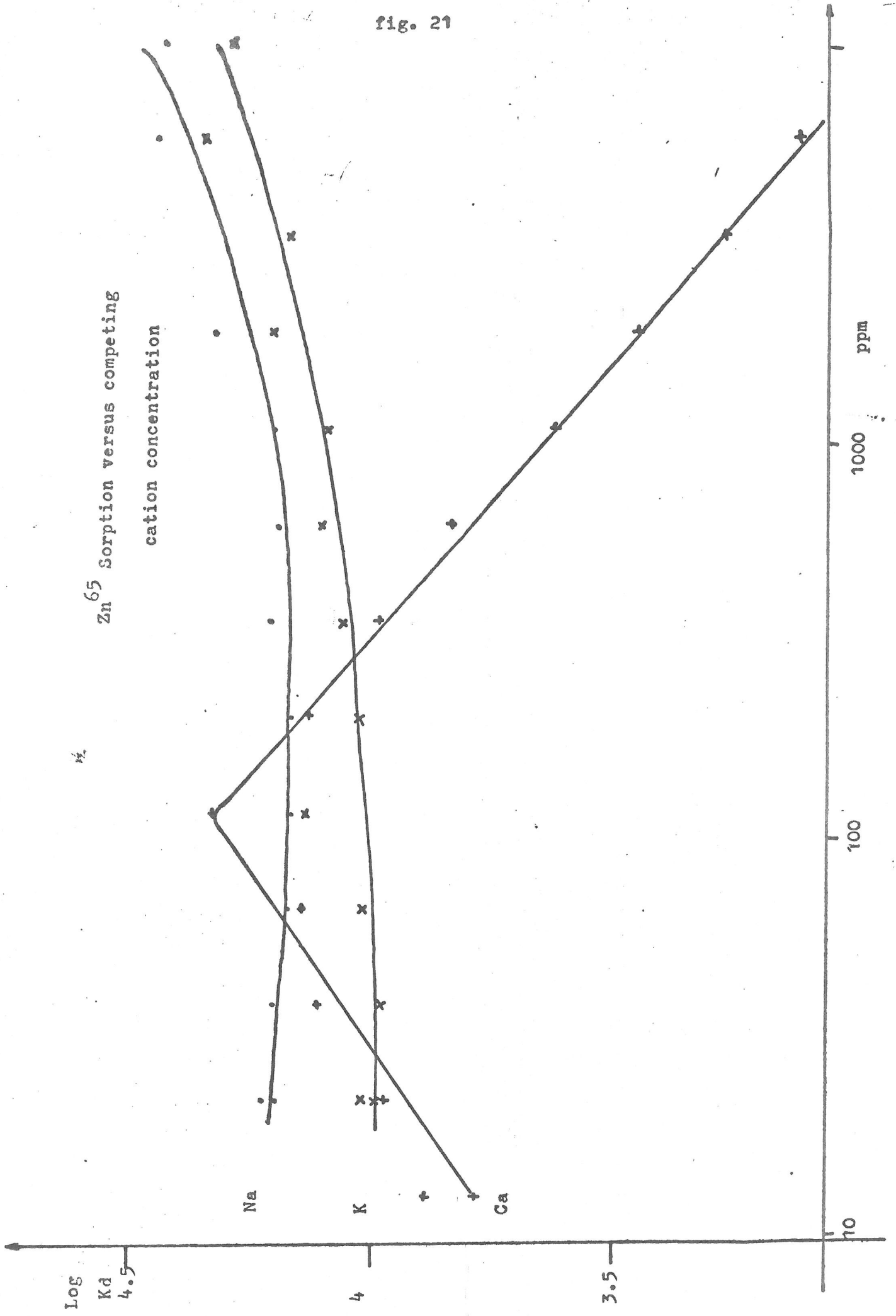


fig. 21



In order to bridge the gap found to exist between capacities determined by 1 N solution and distribution coefficients determined by tracer quantities, we determined Kd in seawater for five specimens with an increasing concentration of the same ion. With Mn<sup>54</sup>, Co<sup>60</sup> and Cd<sup>109</sup>, such influence is considerably less than with Cs<sup>137</sup> which also points to other reaction mechanisms than just a mere exchange of ions (fig. 22, 23, 24 and 25 ).

Fig. 22

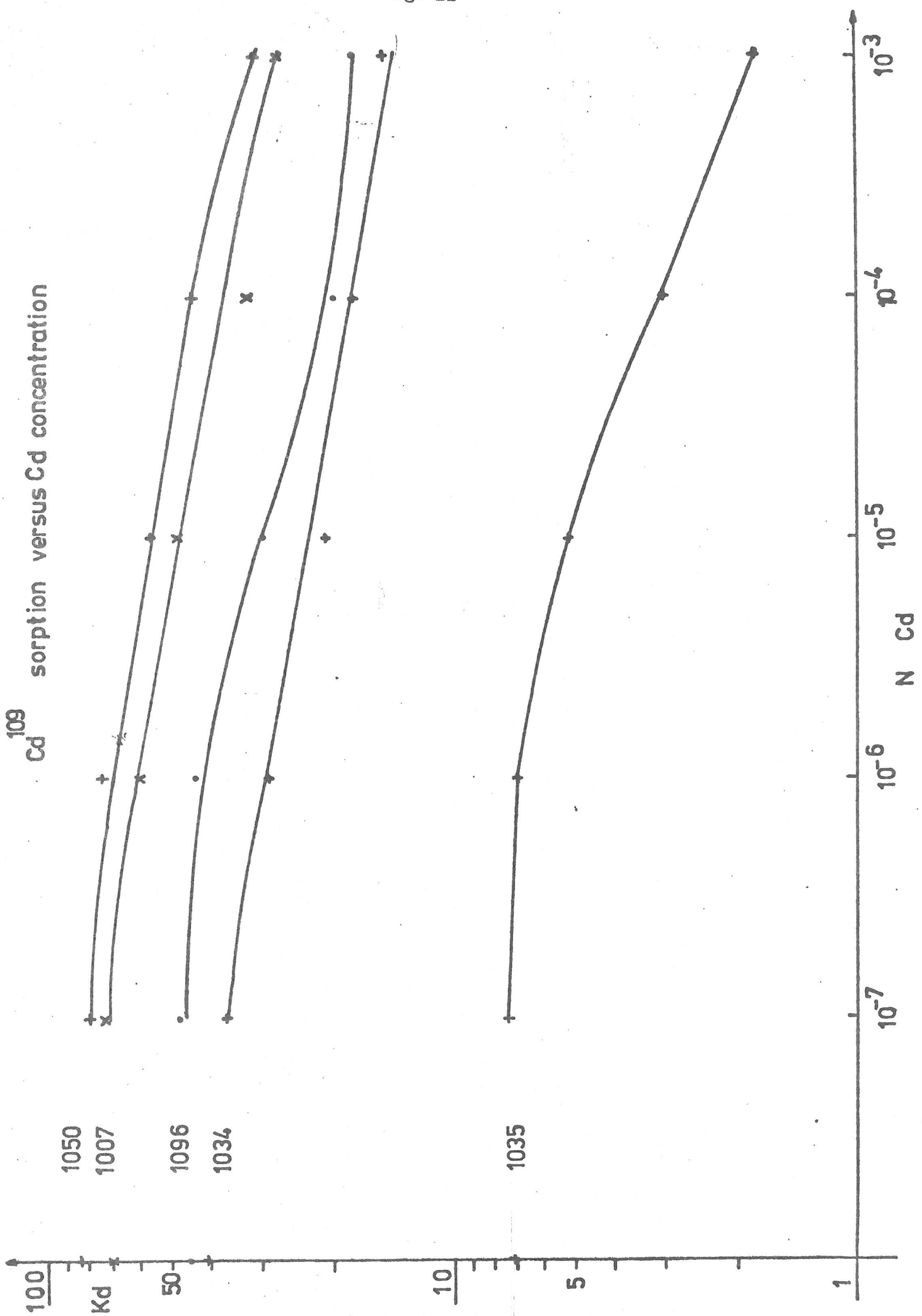




Fig. 23

$^{54}\text{Mn}$  sorption versus Mn concentration

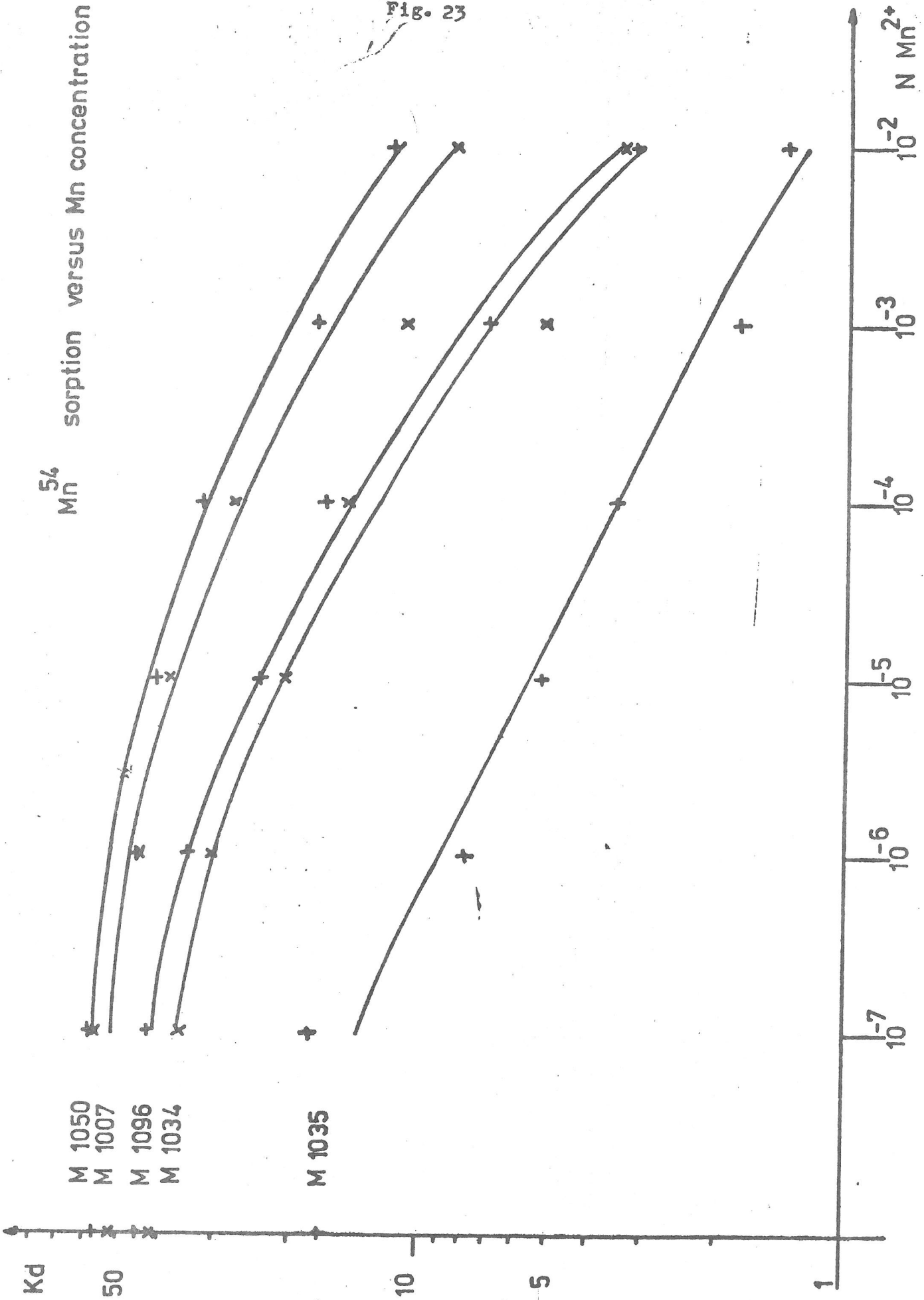


Fig. 24

$Cs^{137}$  sorption versus cesium concentration

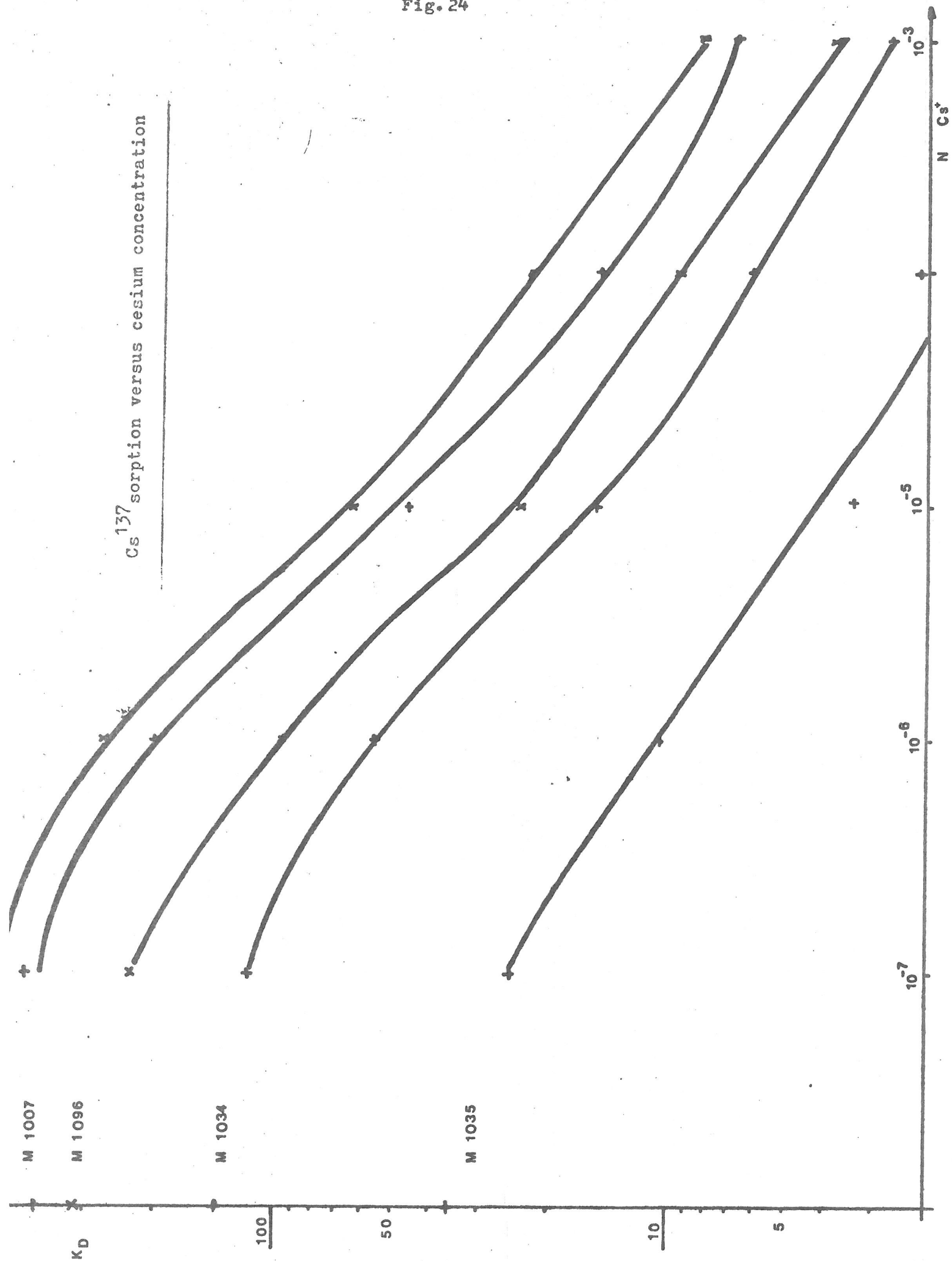
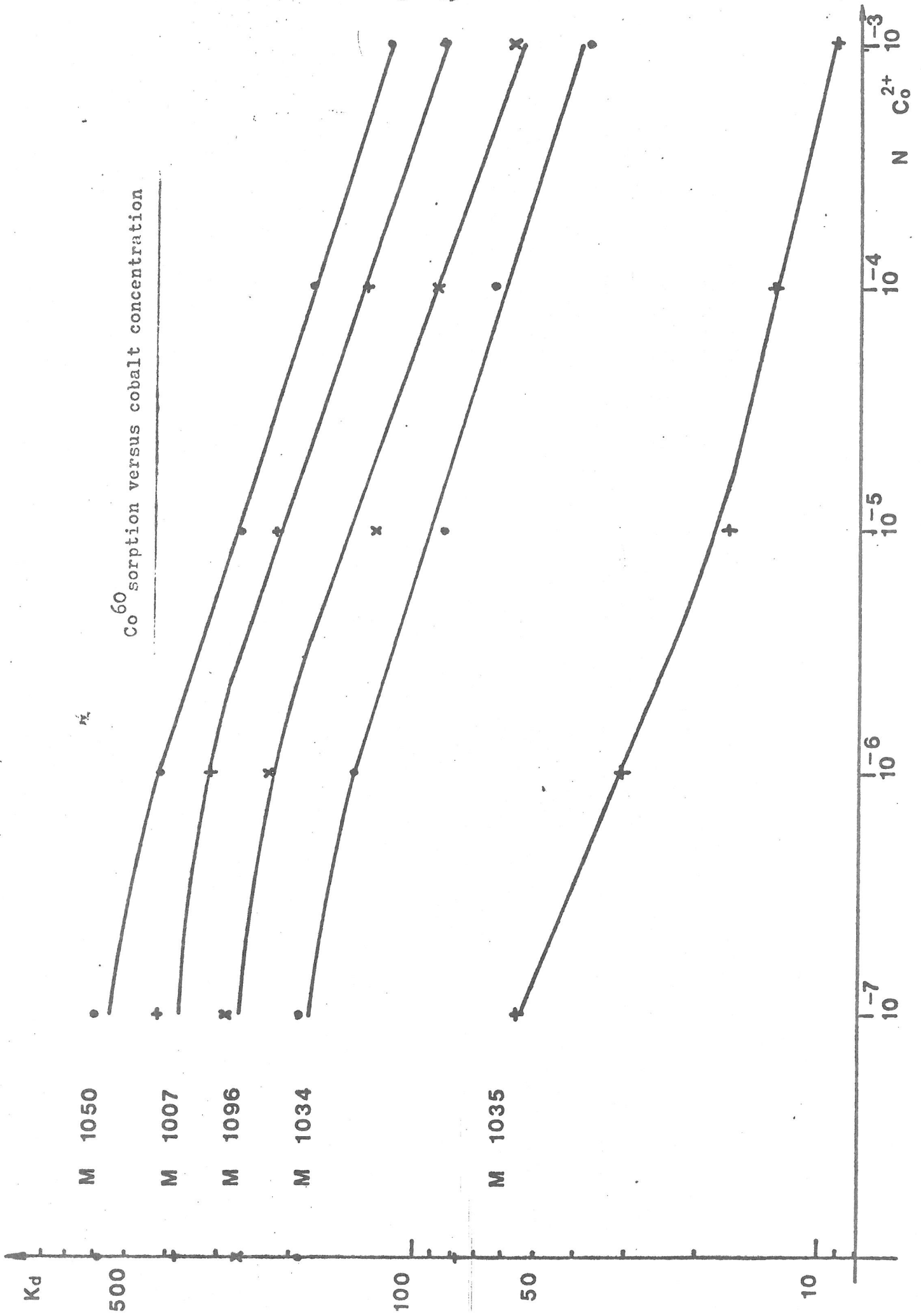


Fig. 25



Supported by literature data and confirmed in our opinion by the tests conducted with sea bottom samples, we may draw the following conclusions.

**Cesium.**-The exchange of ions is probably the dominating phenomenon here. This is confirmed by the strong influence exercised by the other ions in the solution on the sorption of Cs. Although Cs is very easily accepted by silt-rich sediments (  $K_d \approx 20000$  ), the influence exercised by Na and K ions present in the seawater is sufficiently strong to reduce sorption to reasonable limits (  $K_d \approx 400$  ).

**Cobalt.**-Since the influence exercised here by foreign ions is smaller, we find higher  $K_d$  values in seawater. Other phenomena ( formation of  $Co(OH)CO_3$  compounds ? ) will prevail here.

**Strontium.**-This is almost not accepted by the sediments in seawater.  $K_d$  values for all sediments are of the same order of magnitude and all very low. Thus all activity remains here in the fluid phase. Seawater contains approximately  $800 \mu\text{g/l Sr}^{2+}$ . Therefore, some investigators suggest isotopic exchange ( Duursma 1973 ).

**Cadmium.**-Here too, the exchange of ions should be the major phenomenon. The influence exercised by Na and K on the sorption is less marked with regard to this bivalent ion but still greater than with Co and Mn. The sorption in seawater, however, is lower as compared to that of cesium.

Manganese.- Here we probably have a formation of insoluble oxides of Mn which mask possible ion exchange. This would explain the high capacity values.

Zinc.-Zinc features the highest Kd values in seawater, of all elements investigated. We also find a peculiar behaviour with increasing concentration of foreign ions. The exchange of ions can certainly not explain here the behaviour pattern determined and further research will have to be conducted in order to establish which other reactions can better describe the behaviour of zinc.

By excluding strontium from our considerations we may state that all isotopes investigated were better adsorbed by sediments rich in clay or in silt than by sandy sediments. The Kd value provides for the best picture of sorption in seawater.

High concentration of other ions strongly reduces sorption. This is true for all isotopes investigated in seawater. Only zinc and cobalt have high Kd values in seawater.

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