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Soils and oxisols.

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COMPARISON OF ELECTRIC CHARGES IN SOILS FORMED IN A TROPICAL CLIMATE
(GUADELOUPE - MARTINIQUE)

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Introduction

Results for the cation exchange capacity of allophane soils fluctuate greatly because the charges which make up the quasi-totality of the absorbing complex vary.

These variations are mainly due to the method used. This can lead to very serious errors, in the interpretation of soil potentiality. The results can vary from 1 to 3, or more, which changes significantly the percentage of base saturation.

The distribution of charges is modified by the concentration of the reagent, the type of reagent (cations and anions) and the protonic liquids which may be used to eliminate the excess saturating reagent.

Likewise, acid washings and other treatments used in the preparation of the samples can cause significant differences.

Whenever charges are involved, a VERY STRICT operating procedure must be followed, as in the case of cation or cation exchange capacity, extraction of exchangeable cations, determination of exchange acidity etc...

In some allophane soils which have almost no permanent charges, the Zero Point of Charge coincides with the iso-electric point, which permits a better understanding of the distribution of charges.

The Zero Point Charge allows one to select a method where the pH has only a secondary influence.

The Soils

Six soils from Guadeloupe and Martinique were studied :

- 1) Allophane soil without gibbsite -Martinique - Haplotropand
- 2) Allophane soil with imogolite -Guadeloupe - Haplotropand
- 3) Allophane soil with gibbsite -Guadeloupe - Gibbsitic-haplotropand
- 4) Friable ferrallitic soil -Guadeloupe - Oxisol
- 5) Rusty brown halloysitic soil -Guadeloupe - Typic Tropudalf
- 6) Montmorillonitic soil -Martinique - Vertisol

In the case of allophane soils, the pH measured in the KCl and the CaCl₂ are similar. There is little difference with the water pH in the order of 1-2 tenths of unities.

Allophane soil with gibbsite, an old and evolved soil, has low pH: 4,3 ; while younger allophane soils have high pH: 5,8 to 6.

The extraction of iron and aluminium by the TAMM and MEHRA-JACKSON methods does not give any complementary information concerning the variations of Zero Point Charge.

Methods

The techniques of BLOCK-BRUYN (1970) and W.H. HENDERSHOT - L.M. LAVKRULICH (1979) were used with a few minor changes. For the potentiometric measurement of charges, an "indifferent", electrolyte salt of varying concentrations is used : in other words, it does not have a specific absorption which might significantly change the surface properties.

Reagents with a phosphate or silica base should, therefore, not be used for allophane soils.

Electrolyte concentration 0,01 N to 0,2 N were used following the Wada method of the determination of Z.P.C.

Untreated soil or soil in which the organic material has been destroyed or soil subjected to various treatments is used : sodium saturated

Starting with the initial pH or Zero Point Titration, one titrates successively with a base or with an acid of varying concentration.

The different curves obtained in this way cross. The intersection corresponds to the Zero Point of Charge. It is, thus, possible to determine the net surface charge.

Results and conclusion

The Zero Point Charge for allophane soils is very well defined on the graphs :

In contrast, the ZPC for the non-allophane soils (v. ... and brown halloysitic soils) cannot be shown on the graphs.

In the case of the most evolved allophane soil with gibbsite, the ZPC is found at pH 3,9/4,2 ; whereas for allophane soils without gibbsite, the ZPC is found at pH 6,0-6,2 and pH 5,4/5,8 for the sample containing imogolite.

If non buffered reagents are used to determine the exchange capacity, which permits working at the soil pH, there will be less variation with the concentration of reagents than if neutral or basic pH's are used.

The curves clearly indicate that if a basic pH is used, the concentration of the reagent greatly influences both the results and their dispersion.

Diffused by F. Colmet-Daage at the:
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(GUADELOUPE - MARTINIQUE)
Zero Point of Charge of allophane or imogolite soils and oxisols.

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These variations are mainly due to the method used. This can lead to very serious errors, in the interpretation of soil potentiality. The results can vary from 1 to 3, or more, which changes significantly the percentage of base saturation.

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The curves clearly indicate that if a basic pH is used, the concentration of the reagent greatly influences both the results and their dispersion.

If buffered saturating solution are used, the best way seem to determine C.E.C. at different pH value to appreciate variation : generally we have choice : pH 4, pH 7, pH 9, with ammonium acetate.

If the organic matter is destroyed, the negative electrical charges increase. However, this increase in charges is noticeable only in the allophane with gibbsite, the one sample taken from the surface ; all the other samples were taken from the depths.

METHODE

PREPARATION DES ECHANTILLONS

Les échantillons séchés air depuis plus de 2 mois et réduits à 2 mm, sont broyés pour passer sur un tamis AFNOR NF X 11-501 module 28 (ouverture de maille 0.500 mm), afin de minimiser la dispersion des résultats et de permettre un échange régulier.

- Une première partie est conservée pour représenter le sol BRUT,
- Une seconde partie est saturée directement (1) par NaCl Normal, par contact 24 heures avec le réactif puis décantation, centrifugation et remise en contact avec un réactif neuf, 6 fois de suite.

Après la 6^e saturation, et après un contact de 24 heures en salle climatisée à 20° C, on mesure le pH.

Après centrifugation, l'échantillon est lavé alternativement par un mélange eau-acétone (50-50%) et eau-méthanol (50-50%) (3 fois) pour éliminer l'excès de cation saturant. Un lavage à l'eau uniquement entraînerait des risques d'hydrolyse. La qualité du lavage est testée au nitrate d'argent. Les échantillons sont mis à sécher à l'air, puis à l'étuve à ventilation à 40° C et rebroyé au tamis de 0,5 mm.

- Une troisième partie est traitée par H₂O₂ à 80° C pour détruire la M.O. La destruction est incomplète mais s'avère suffisante pour éliminer les formes relativement libres et extractibles. En effet, la M.O. dans les sols volcaniques forme des complexes très stables.

(Le traitement par NaOCl provoque une élévation de pH qui semble supérieure à celle de H₂O₂ et risque d'être préjudiciable dans le cas de gels amphotères, sans pour cela apporter une destruction très poussée. On peut toutefois craindre, dans les deux cas, la refixation des formes de Al liées à la M.O. détruite et une hydrolyse qui peut modifier la nature de Al dans l'échantillon).

Après destruction, l'échantillon est saturé par Na comme ci-dessus et le pH des échantillons ajusté au même niveau que ceux du traitement précédent par addition successive de réactif dilué acide ou basique. Cet équilibre demande 3 à 4 jours. L'échantillon est lavé, séché et rebroyé au tamis de 0,5 mm.

Tous les pH sont pris avec une électrode combinée, dans la suspension de sol avec agitation magnétique continue à vitesse réduite, pour éviter un effet Vortex trop important et l'introduction d'air dans le milieu.

DOSAGE

La mesure des ions H⁺ et OH⁻ absorbés ou déplacés est effectuée, d'une part sur un potentiographe METROHM, avec burette automatique et agitateur magnétique incorporé pour les courbes complètes pH 3.0 à 10 environ, d'autre part et simultanément, sur un pHmètre-ionomètre ORION 701 A relié à un enregistreur GOERZ avec une échelle expansée pour la détermination de la zone de croisement des courbes.

Le point 0 de titration (ZPT) est pointé sur la courbe lors des titrations acide ou basique. Il correspond au pH de départ des échantillons traités ou non traités (sur sol BRUT l'addition de NaCl provoque un déplacement rapide de l'origine).

Le Zéro Point Charge (ZPC) qui est atteint lorsque la charge nette totale est égale à 0, est déterminé par titrage relativement lent, au moyen d'acide chlorhydrique ou d'hydroxyde de sodium N/20 dans un milieu d'électrolytes "indifférents" (NaCl 0.001N, 0.01N, 0.05N, 0.2N) c'est-à-dire, ne présentant pas de fixation anionique préférentielle indésirable.

Na⁺ a été choisi de préférence à Ca²⁺, surtout en raison de la facilité d'utilisation de HCl et NaOH, mais aussi à un degré moindre, en raison des irrégularités que pourraient introduire dans un dosage relativement lent les pressions partielles de CO₂ sur les sels de Ca.

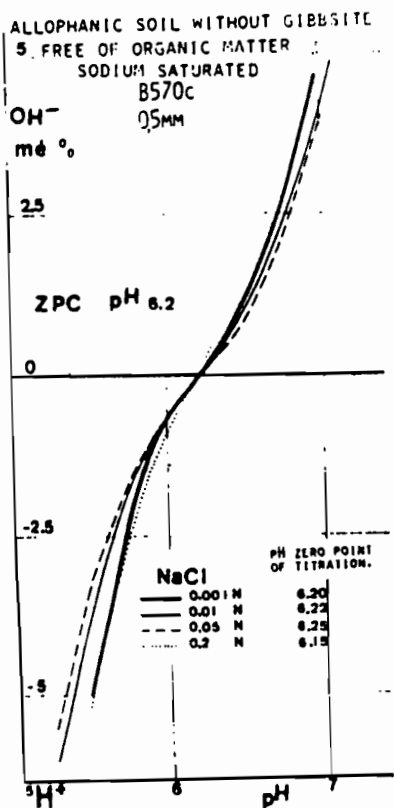
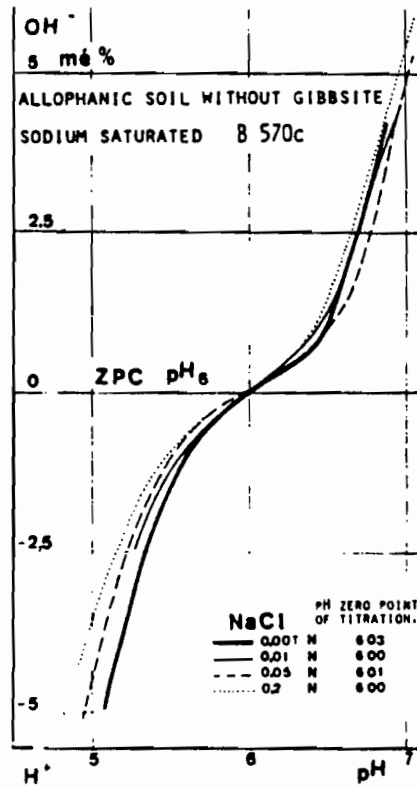
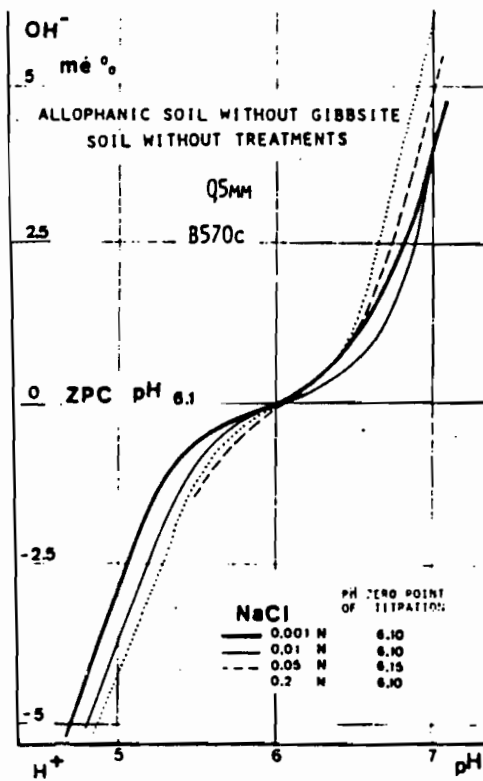
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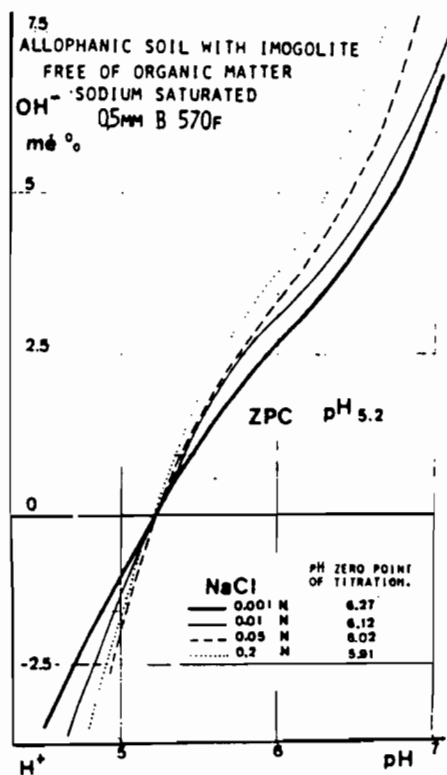
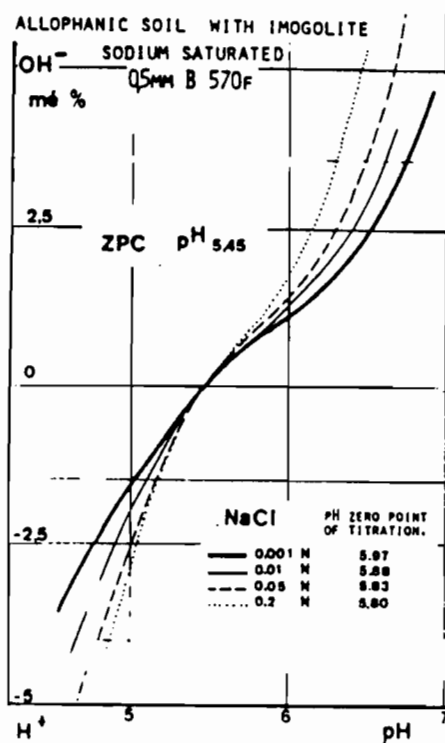
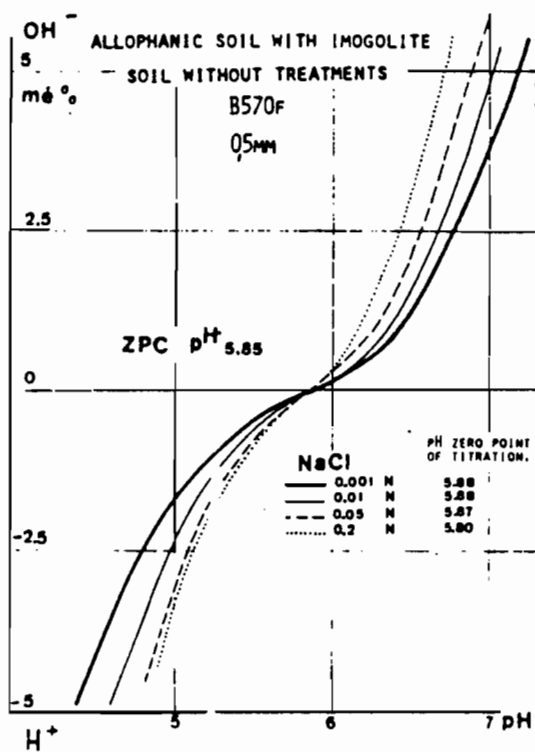
- 2g de sol broyé à 0.5 mm (traité ou non traité) sont mis en contact avec 40 ml de NaCl de concentration "x", puis l'échantillon est titré par HCl N/20.

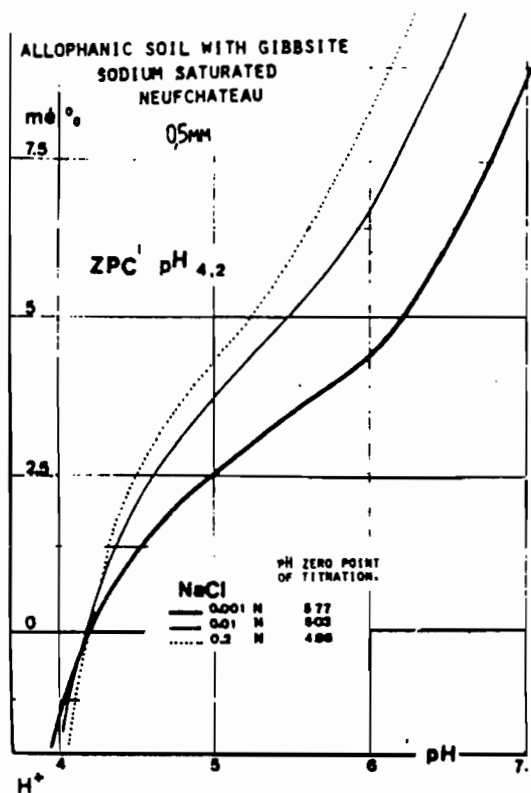
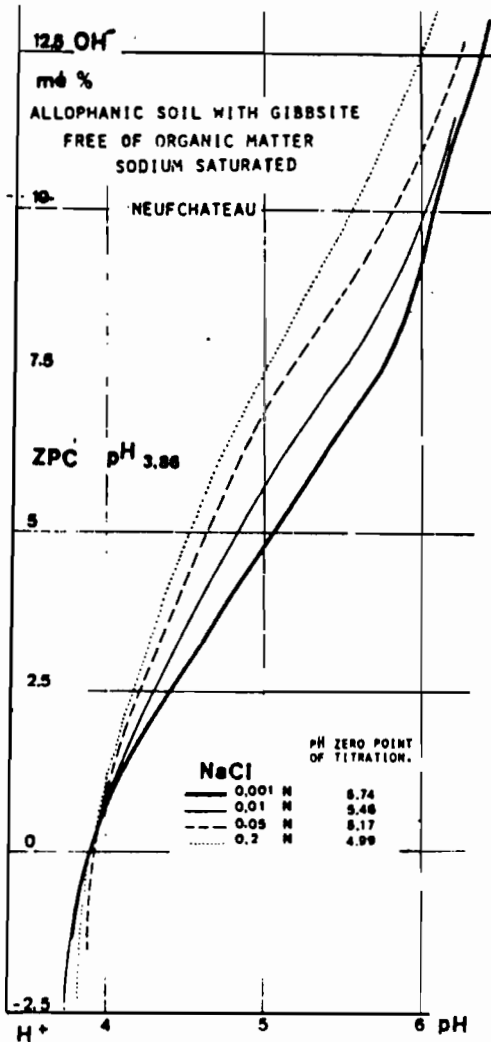
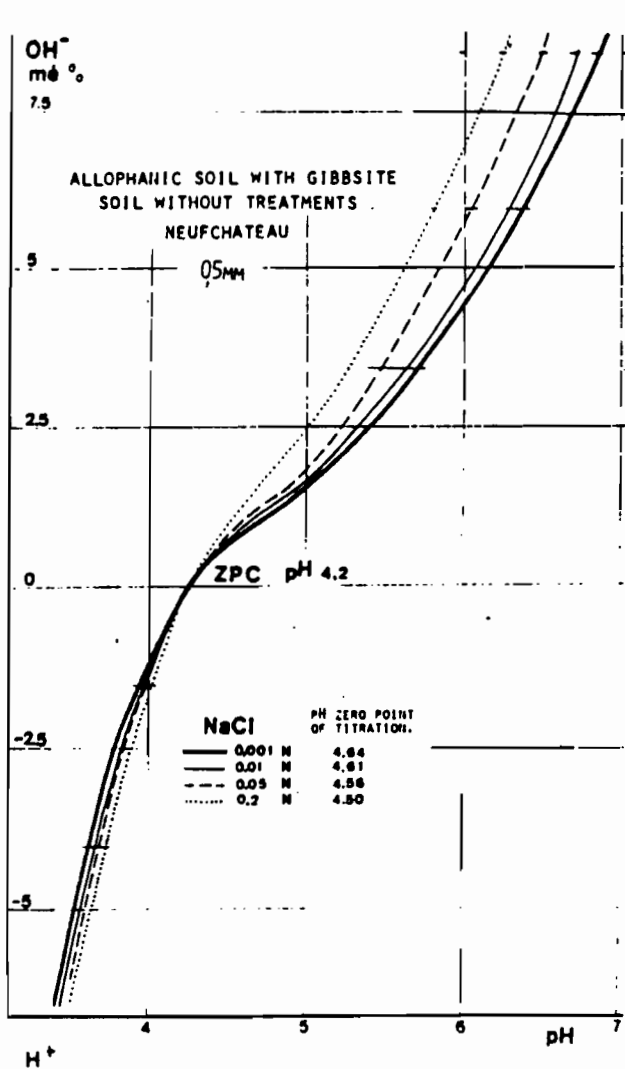
- Sur une autre prise, on procède au titrage par NaOH N/20, en utilisant un récipient permettant d'obtenir un contact avec le CO₂ de l'air le plus réduit possible.

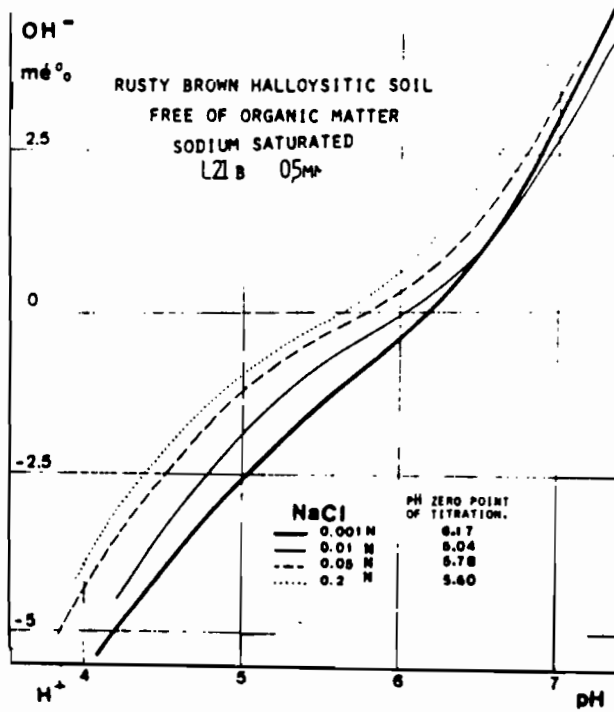
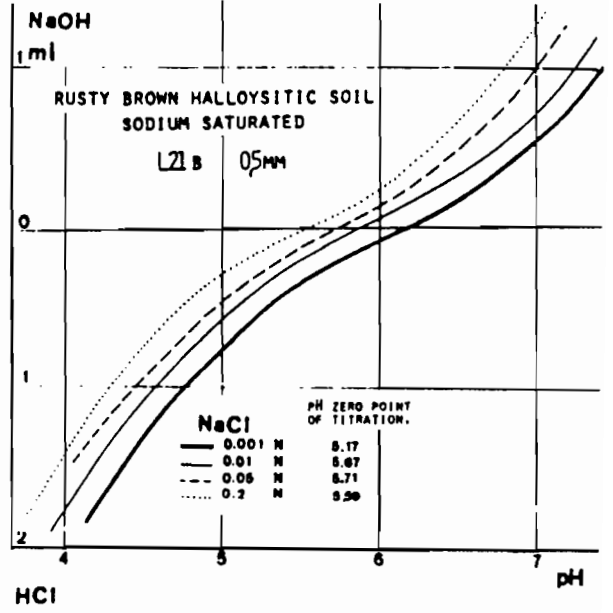
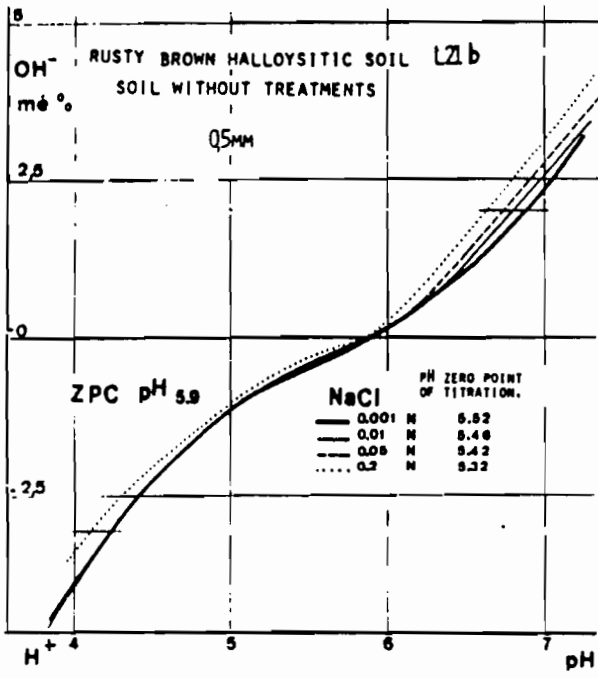
Les dosages sont effectués ensuite dans les mêmes conditions, en présence de 40 ml de NaCl des 3 autres concentrations. La vitesse est de 20 ml en 200 mn, soit une addition continue de 0.1 ml/mn.

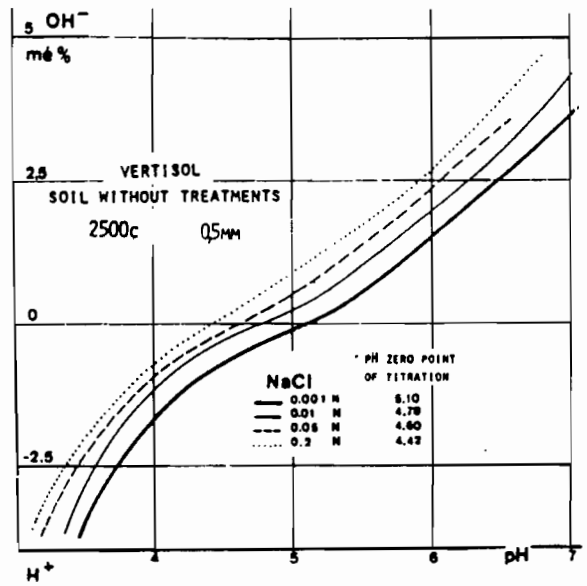
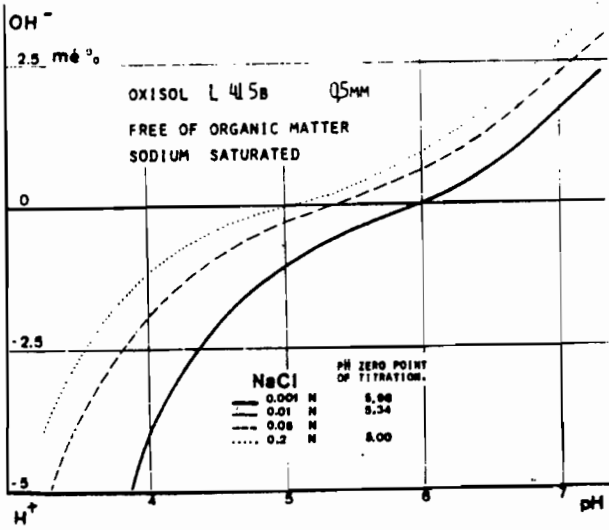
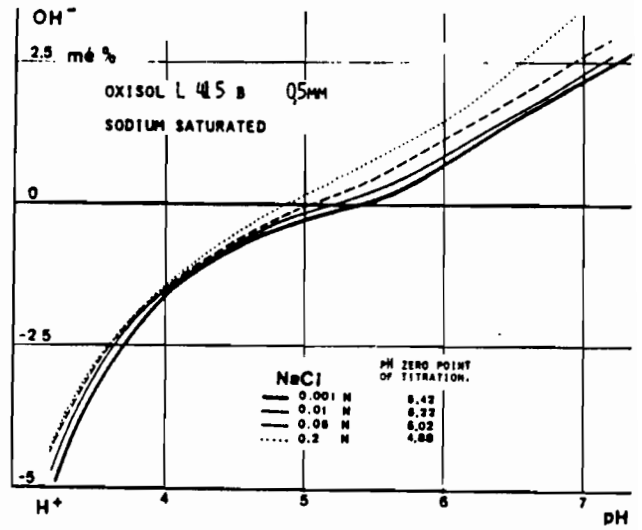
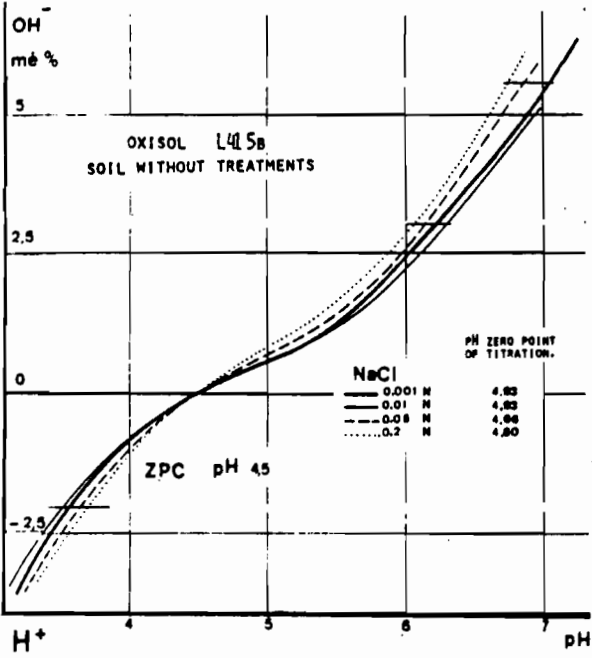
Le point de recouplement des courbes indique le ZPC. Le point de croisement peut se faire au-dessus ou au-dessous du ZPT. Les résultats sont calculés en mEq d'acide ou de base absorbés et la valeur de ZPC et les charges q₊ déterminées sur la bande d'enregistrement à défilement constant.

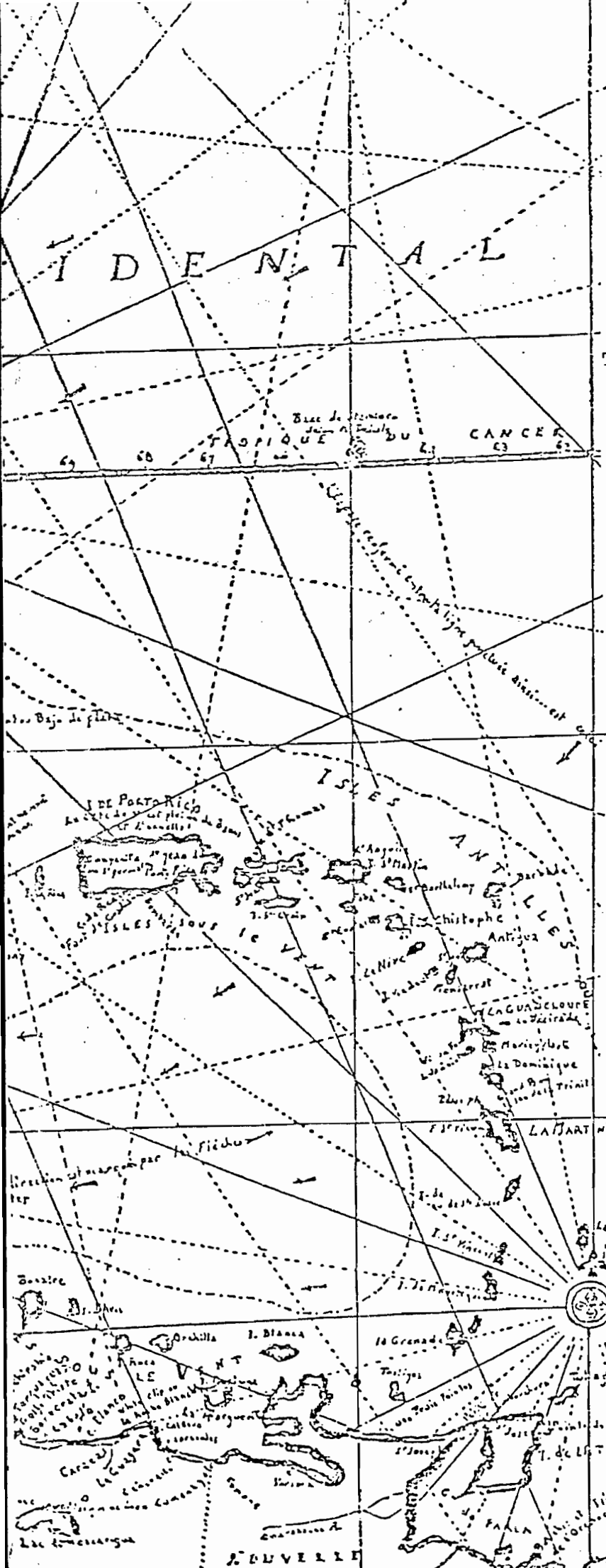












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Contributions au
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