

Division des Sols



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No. 400

Calcium - Magnesium

Potassium-Sodium

Analyse des Sols, Des Eaux et des Plantes

Damas

LE CENTRE ARABE
POUR LES ETUDES DES ZONES ARIDES ET DES TERRES SECHES
(ACSAD)

The Arab Center
for the Studies of Arid Zones & Dry Lands

- Soil Division -

No. 400

Calcium - Magnesium

Potassium-Sodium

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Résumé (Français)

Un documentation bibliographique commentée sur les méthodes utilisées dans l'analyse des sols des plantes et des eaux des zones arides est présentée. Elle est destinée aux laboratoires d'analyse de routine ou de recherche. La présentation des résumés d'articles fait ressortir la technique employée. Le matériel et les produits utilisés par les auteur ainsi que les figures et les tableaux apparaissant dans le texte original. Cette documentation est remise à jour au fur et à mesure que de nouvelles references sont disponibles dans la collection du laboratoire de l'ACSAD. Les articles sont résumés soit en Français soit en Anglais.

Résumé (Anglais)

These abstracts cover the methodology of the analysis of soil water and plants with special reference to arid zones environment. They are intended to provide the laboratories with an informative tool on methodology. Emphasis is made on the technique, scientific equipment and chemicals used in each original paper reviewed. These abstracts are updated as soon as sufficient material is collected in the reference collection of ACSAD to justify a new edition. Papers are abstracted in French or English.

- Mots Clés:

Authors : ADAMS (J.M) & EVANS (S)
Title : Determination of the cation exchange capacity (layer charge) of small quantities of clay minerals by nephelometry.
Public : Clay & Clay Mineral 2-27-1978.
Pages/ref: 137-139 / 7 ref.

Summary:

Irreversible cation fixation on clay prevents the Ca determination of CEC of clay when less than 30 mg of sample is available and only layer charge may be measured directly.

Method: 30 mgr of Ca or Ba-saturated clay is fused with 0.7g NaOH to red heat 10 min. and dissolved in HCL (final conc.: 4%).

Barium: To 5ml of the clay solution, 5ml of glycerol/ethanol mixture and 2.5ml of (1.5M) H₂SO₄ are added, volume is made up to 25ml. Turbidity is measured after 10 minutes.

Calcium: To 5ml of the clay solution add 4.0ml of the glycerol/ethanol mixture, 1.5ml 3M NH₄OH and 4.0ml oxalic acid solution (20 g/l) turbidity is measured after 25 min. Authors suggest that barium may be fixed on surface of clay particles and propose to use Ca saturated samples even if the quantity of available clay is only 5 to 30 mgr.

Tables : Comparison of nephelometric and others determination of CEC (on Ba and Ca-saturated clays) for bentonite, montmorillonite and beidellite samples.

Precision: For 30 mgr samples having a CEC 70-100 meq/100 gr. duplicate measurements agreed within 10% and comparison with other methods was better than 5%.

Chemicals: NaOH . NaCl . HCL . Glycol . Ethanol . Amonia . Oxalic acid.

Key Words: CEC / MINE / Ba / Ca /

Author : ALLEN (S.E)
Title : Metallic elements in soils: Determination of Ca, Mg, Mn,
K and Na in soils.
Public : Pye Unicam Ltd.
Pages/ref: 3 pages / 1 ref.

Summary:

Soil was extracted either with ammonium acetate N or 2,5% acetic acid. Lanthanum was added to overcome interference from aluminium, silicon, phosphorus in the determination of (Ca, Mg). Preparation of standard solution was described.

Manganese, potassium and sodium standard solutions are prepared as a mixture of each element (range 0 - 2,5 - 5,0 mgr/l) in ammonium acetate or acetic acid.

Calcium and Magnesium standards are prepared in mixed solutions (0 to 10 ppm Ca and 0 to 0.5 ppm Mg) in 1% sulfuric acid, and either / M ammonium acetate or acetic acid.

Addition of sulfuric acid to unknown reduces the amount of lanthanum required.

Sodium and potassium are determined by flame emission. Calcium at 422,7 nm, magnesium at 285,2 and manganese at 279,5. Instrumental conditions were given in detail.

Tables :- Dilution tables for stock solutions of Ca and Mg.
- Instrumental setting (SP 1900).
- Comparison of duplicate determination with reference values on three samples. (Extraction of exchangeable plus labile, plus soluble Ca, Mg, Na, K, Mn was done with ammonium acetate N and with acetic acid 2,5%).

Material : AA Spectrophotometer . Ca, Mg, Mn Hollow Cathod Lamp.

Chemicals: Calcium carbonate . Mg ribbon . Mn metal . Sodium chloride . HCL . Potassium chloride . Lanthanum 0.4% . Acetic acid . Ammonium acetate . Sulfuric acid .

Key Words: CALCIUM / MAGNESIUM / MANGANESE / POTASSIUM /
SODIUM / AAS /

ALLE

Auteur : xxx / ARIANA
Titre : Dosage du calcium et du magnesium dans les eaux, les extraits de sols et les bases échangeables à l'aide du complexe III.
Public : Methodes d'analyse des sols et des eaux appliquées au laboratoire de l'Ariana - DRES Tunis.
Pages/ref: 6 pages / 3 ref.

Resume:

Le calcium est déterminé à PH12 par EDTA M/50 par virage du violet au rose de murexide. La somme (calcium + magnesium) à PH10 jusqu'à virage au bleu du colorant noir d'eriochrome. La fin du virage peut être suivie par une cellule voltaïque et une filtre à 530 nm (calcium). La concentration en magnesium est obtenue par différence.

Les ions gênants sont complexés par du cyanure de potassium ou de la triéthanolamine.

Methodes: Calcium

25 ml prise d'essai plus, 2 ml triéthanolamine + 3 gouttes murexide 0.2% dans méthanol, 8 ml NaOH 2,5 N virage du rose au violet.

Calcium + Magnesium

25 ml prise d'essai plus 2 ml triéthanolamine (ou cyanure de K) plus 6 gouttes d'indicateur plus 2 ml tampon titrer avec EDTA M/100 jusqu'au bleu cobalt.

Indicateur (Ca + Mg):

0.2 gr noir d'eriochrome T, 2 gr chlorhydrate d'hydroxylamine ajuster à 50 ml par méthanol.

Tampon PH 10: 67,5 gr de chlorure d'ammonium dissous 200 ml H₂O, ajouter 570 ml d'ammoniaque concentré, compléter à 1.000 ml. Vérifier PH 10.

Figures :- Montage pour détection photométrique de la fin de virage.
- Table de calcul des concentrations.

Precision: Titrage valable pour n'importe quel milieu.

Produits : Murexide . Méthanol . Triéthanolamine . Chlorure d'ammonium . Ammoniaque . Chlorhydrate d'hydroxylamine . Noir d'eriochrome . Sulfate de magnesium .

Mots Cles: CALCIUM / MAGNESIUM / EAUX / SOLS / TOTAUX / ECHANGEABLES /

ARIA

Author : BOUMANS (J.H)
 Title : Alkalinity aspects of leaching of salts affected soils.
 Public : In: Reclamation of salt affected soils in Iraq.
 I.I.L.R.I. Wageningen 1963 (Dieleman ed.).
 Pages/ref: 48 to 56 / 49 ref.

Summary:

South of Baghdad the soils of Tigris and Euphrates plains are saline (estimated average ESP 20 to 25). Gypsum is present in ~~most~~ sub-soils and 20 to 30% of fine are found commonly. The behavior of soils during leaching was studied in field experiments. Relationship were developped, (a) between soil salinity as measured in 1/2 extract, pH and exchangeable sodium at different levels of ESP (from 0 to above 30), (b) between ESP and Ec of 1/1 extract at constant pH. On the soil submitted to experiment, the alkalinity may be predicted by performing two simple tests pH and Ec and using the relation developped in the paper.

Tables : - Composition of Tigris water (Baghdad 1949)
 - Average infiltration rate for 10 soils (0-250 cm depth).
 - Soil analysis after leaching tests.
 - Decrease of Exchangeable sodium and salt during leaching.
 - Relationship between ESP, pH and salinity.
 - Relationship between soil salinity and Exchangeable Na (pH 7.8).

Key Words: SALINITY / EXCHANGEABLE SODIUM /

Authors : CHANG (P.C) & VAN SCHAİK (J.C)
Title : Automated method for soil salinity studies.
Public : Technicon Symposium "Automation in Analytical Chemistry".
New York, Sept. 10-1965.
Pages/ref: 94-95 / 3ref.

Summary:

Soil salinity is estimated by calculating exchangeable sodium percentage (ESP) from the values of Ca, Mg, Na concentrations in the saturation extract of the soil sample. The paper presents simultaneous determination of Na⁺ and (Ca⁺⁺ + Mg⁺⁺) in an autoanalyser assembly including a colorimeter, a flame photometer and a double-pen recorder. The results obtained are compared with a direct flame photometric method for Na and with volumetric titration with Eriochrome Black T for the sum (Ca⁺⁺ + Mg⁺⁺).

Figures : - Flow diagram (16 tubes).
- Concentrations of Na and (Ca+Mg) in soil extracts as found by different methods: (a) for EC less than 1.3 mS, (b) for EC greater than 1.3 mS.

Precision: Max. concentration of the sum calcium plus magnesium is 100 meq/l with the flow system adopted.

Equipment: Continuous flow colorimeter ; peristaltic pump (16 positions) ; dialyzer ; "in-line colorimeter ; two-channels flame photometer ; two pen recorder.

Chemicals: Lithium nitrate - Na₂Mg EDTA - Ammonium chloride - Calgamite - Indicator - NaCl - MgCl₂.

Key Words: SALINITY / CONTINUOUS FLOW COLORIMETRY /

CHAN

Auteur : CLEMENT (A)
 Titre : Etude de la corrélation entre trois méthodes de quantification du K chez les végétaux.
 Public : Bulletin de l'ENSAIA, Tome XXI, Fascicule I-II 1979. Nancy.
 Pages/ref: 29-36 / 5 ref.

Résumé:

Sont étudiés l'émission et l'absorption atomique du potassium à 766.5 nm et l'émission à 404.4 nm. Les échantillons soumis à l'analyse proviennent d'Épicéa (Picea excelsa Link) et de pin noir (Pinus nigra nigracians). Soixante dix-neuf échantillons contenant de 0.1 à 0.6% de K sont analysés et les résultats traités statistiquement.

Méthode: 500 mg de végétal sont minéralisés avec 12 ml H₂O₂ et 10 ml HClO₄. Le volume après minéralisation est ajusté à 100 ml. Les échantillons sont dilués 2/10^e à 766.5 nm et non dilués à 404.4 nm.

L'émission donne en moyenne de résultats supérieurs de 5% à l'absorption atomique, l'écart étant d'autant plus grand que la teneur en K est plus petite.

L'absorption atomique à 766.5 nm et l'émission à 404.4 nm donnent des résultats identiques. Cette dernière méthode est donc intéressante car elle permet d'analyser directement les solutions de minéralisation sans dilution. De plus elle ne nécessite pas de lampe à cathode creuse.

Tables/Precision:

- comparaison entre emission (y) et absorption (x) à 766.5 nm
 $y = 0.77 + 0.94x$ (r=0.994)
- comparaison entre emission à 404.4 (z) et absorption à 766.5 nm
 $z = 0.129 + 0.987x$ (r=0.966)
- comparaison entre emission à 404.4 nm (z) et 766.5 nm (y)
 $z = 0.645 + 1.043y$
- Résultats du dosage du potassium suivant les trois méthodes pour 79 échantillons.

Mots Clés: POTASSIUM / A.A. PRECISION/

Authors : ELSEEWI (A.A) - ELATTAR (H.A) & DAOUD (A.M)
 Title : Relationship between soluble and exchangeable sodium in some soils of the Nile Delta: An examination of the SAR concept.
 Public : Soil Science 124-4-1977.
 Pages/ref: 249-264 / 8 ref.

Summary:

The SAR parameter (sodium adsorption ratio, or $1.414\text{Na}/(\text{Ca}+\text{Mg})^{1/2}$ where concentrations are expressed in meq/l in the saturation extracts) is an easy way to estimate ESP, (exchangeable sodium percentage) providing the relationship between ESP and SAR is general. This relationship is examined in 31 surface-soils from the Nile Delta and compared with data obtained earlier with different soils. Soluble plus exchangeable cations are measured in NH_4OAC pH 7.0 for Na and K and NaOAC pH 8.2 for Ca and Mg; results of exchangeable cations are given after subtracting the corresponding values found in saturation extract.

Regression equations are calculated first between SAR and ESR and then between SAR and ESP ($\text{ESR}=\text{ES}/(\text{CEC}-(\text{ES}+\text{EK}))$) over a wide range of ESP values.

Observed values (from soil analysis) and calculated values are compared and discussed for 31 soils.

Tables : 1. Location of sampling sites in the Nile Delta.
 2. Chemical and physical characteristics of the soils studied.
 3. Relationship between SAR and ESR.
 4. SAR in relation to calculated ESP and to observed ESP.

Precision: $\text{ESR} = 0.0273 + 0.01457 \text{ SAR}$ ($r = 0.934$) Author's
 $\text{ESR} = -0.0126 + 0.01475 \text{ SAR}$ ($r = 0.923$) U. S. Sal.
 $\text{ESR} = 0.0057 + 0.0173 \text{ SAR}$ (Bower's)

Chemicals: Those necessary for CEC and for Na, K, Ca, Mg analysis and extraction.

Key Words: SALINITY / CEC / EXCHANGEABLE SODIUM /

ELSE

Auteur : FILLMAN (G)
 Titre : Les méthodes de titrimétrie semi-automatique utilisées au laboratoire de pédologie appliquée des S.S.C de Bondy.
 Public : ORSTOM 1971.
 Pages/ref: 84-95

Résumé

La méthode présentée est une méthode complexométrique automatique pour la détermination de Ca^{++} et $\text{Ca}^{++} + \text{Mg}^{++}$ dans l'extrait du sol dans un laboratoire d'analyse de routine. Pour le dosage de Ca^{++} 5 ml de l'extrait est amené très exactement à pH 12.5 en utilisant NaOH 20 N et 2ml de CNK 1% + 0.25 ml de calcon (1). Le Ca^{++} est dosé en utilisant complexon N/50, l'appareillage utilisé comprend un colorimètre, une burette à impulsion et un enregistreur potentiométrique.

Détail des colorants utilisés:

- a) pour le Ca seul: 0.2 gr Calcon, 25 ml TEA, complété à 100 ml avec le MeOH.
- b) pour la somme (Ca+Mg). 0.2 gr de noir d'ériochrome T plus 0.1 gr de chlorhydrate d'hydroxylamine dans 50 ml de MeOH (stabilité: 8 jours). En cas où l'échantillon est pauvre en $\text{Ca}^{++} + \text{Mg}^{++}$ on utilise le complexon III N/50, le pH de l'extrait est ajusté à 10.5. Lanthanium détermination pour $\text{Ca}^{++} + \text{Mg}^{++}$ est faite en utilisant un filtre de 660 mμ.

Figures : Photographies et schémas des montages utilisés:
 - exemples de courbes avec solution étalons,
 - exemples avec extraits de sol.

Matériel : PH mètre - Burette automatique à impulsion - Enregistreur potentiométrique couplé à la burette à impulsion. Colorimètre avec sortie enregistrement.

Produits : Complexon III ; Solution Ca^{++} ; NaOH ; CNK ; Calcon solution Mg^{++} ; NH_4Cl ; Triethanolamine ; NH_4OH Eriochrome T.

Mots Clés: CALCIUM / MAGNESIUM / TITRIMETRIE AUTOMATIQUE /

Authors : FLANNERY (R.L) & STECKEL (J.E)
 Title : Simultaneous determination of Ca, K, Mg and P in soil
 electro-dialyzates by autoanalysis.
 Public : Technicon/ Soil and Crop Dept. Duttgers, State University.
 Pages/ref: 11 pages / 21 ref.

Summary:

Calcium and Potassium are simultaneously determined in a twin flame photometer system. Magnesium and Phosphorus are measured by simultaneous colorimetry through two colorimeters.

Flow chart for feeding liquids to flame photometer is:
 Sample (2.9) / air (1.2) / HCL N (1.2) / single mixing coil /
 lithium nitrate 7,5 meq/l (1,6) / double mixing coil / debubler
 (6.1) to waste - (0.8) to flame photometer, (625 nm for Ca and
 760 nm K).

Flow chart for colorimetry of Magnesium:
 Sample (0.8) / air (0.8) / diluent Brij 35, 0.4% (2,9) / single
 mixing coil / debubler T to waste (2.0) / remaining stream
 (i.e 25 ml) is repumped diluted by (2.5) polyvinyl alcohol 0.2% /
 air (0.8) / mixing coil / magnesium blue 0.02% (0.8) / NaOH 2N
 (2.5) / 2 minutes delay coil / colorimeter 625 nm / repump to waste
 (6.6) / .

A drift of baseline is reported if concentration of Mg is more than 5 ppm.

For phosphorus: Sample (0.8) / air (1.6) / distilled water
 (2.9) / mixing coil / debubler to waste (2.4) / remaining 2.0 re-
 turned to pump / air (0.8) / chloromolybdic acid 1.5% (0.8) /
 mixing coil / stannous chloride 0.005M (0.42) / debubler to waste
 (2.42) / remaining stream (2.5) pumped to colorimeter 660 nm /
 repump to waste (2.5) / .

Tables :- Standard errors of autoanalysis on Ca, K, Mg, P determined in
 0.05N boric acid.

- Flow diagrams for (Ca, K), Mg and P.

Range : Ca: 2.5 to 150 ppm, K: 0.5 to 25 ppm, Mg: 1 to 10 ppm,
 P : 0.15 to 4 ppm (in solution without dilution).

Material : Two continuous flow colorimeters systems.
 Dual flame photometer - Two recorders (double pen).

Chemicals: 1. Ca, K: Calcium carbonate . Potassium chloride . HCL .
 Boric acid . Lithium nitrate .
2. Mg : Magnesium blue . N,N'- dimethylformamide . Polyvinyl
 alcohol . Brij 35 . NaOH . Magnesium sulfate .
3. P : Amonium molybdate . Stannous chloride . Disodium
 hydrogen phosphate.

Key words: CALCIUM/POTASSIUM/MAGNESIUM/PHOS/AUTOANALYSE/

FLAN

Authors : FRITZ (J.S) , WAKI (H) & GARRALDA (B)
Title : Anion exchange separation of Calcium and Strontium.
Public : Analytical Chemistry 4-- 36 - 1964.
Pages/ref: 900 - 903 / 8 ref.

Summary:

Separation of calcium, magnesium, strontium is achieved through anion exchange resin. Elution by 0.25 M nitric acid - 95% methanol (or 95% ethanol).

Method:

Anion exchange resin (60 to 100 mesh) is converted to nitrate form by nitric acid. Resin column is 22 cm by 1 sq.cm section. Resin is poured in 95% methanol. Column is pretreated by passing 40 ml 0.25M nitric acid in 95% ETOH (solution E), then 30 ml sample. Elution with 0.5 to 0.6 ml/min solution E. Magnesium is eluted in the first 80 ml. Eluent is changed to 0.25M nitric acid in 95% MeOH and calcium is eluted by 70 to 100 ml (depending of Ca / Si ratio). Strontium is then eluted by 50 ml MeOH (or water). Column is washed by dilute nitric acid.

A 10 ml column is sufficient for separation of magnesium and calcium only.

Tables :- Elution curve for Ca, Sr in ethanol.
- Elution curve for Ca, Sr in methanol.
- Comparison of various effluents.
- Quantitative separation of Sr from Ca and Mg.
- Elution behavior of Mg and Ca in heavy loading (1 millimole).
- Elution curve for Mg, Ca, Sr separation.

Precision: Recovery percentage is 0.5 to 1.2% in the range of 0.1 to 0.5 millimoles added (i.e 8 to 40 meq/l in solution).

Material : Ion exchange column.

Chemicals: Methanol . EDTA . Anion exchange resin . Amberlyst XN-1002 . Magnesium nitrate . Calcium nitrate . Strontium nitrate . Nitric acid .

Key words: CALCIUM / MAGNESIUM / WATER / RESIN /

FRIT

Auteurs : GREYER (C) & BRUTTEL (P)
 Titre : Titrage du Ca et Mg en presence individuelle ou commune par voie de complexation a l'aide d'electrodes polarisees.
 Public : Metrohm No. 56 f.
 Pages/ref: 3 pages / 5 ref.

Resume:

La fin de reaction des dosages complexometriques de Ca et Mg a l'aide de reactifs comme EDTA ou EGTA est determinee par methode voltametrique et par electrodes polarisees a courant alternatif impose.

Methode 1: Titrage voltametrique:

20 ml d'echantillon + 10 ml tampon (6.1 gr d'ethanolamine/l dans HNO₃ dilue a PH 10,5). On titre le calcium par la solution EGTA et le sodium par EDTA, avec un courant de polarisation de 1 micro A.

Methode 2: Electrodes polarisees a courant alternatif:

Les electrodes sont polarisees a courant alternatif par le conductiscope E 365B a 10 microampere le rapport Mg / Ca peut aller de 10 a 100.

Precision: Methode 1: sensibilite 0.1 ppm Ca et 0.6 ppm Mg (avec une erreur de 5%), l'erreur est inferieure a 1% pour des teneurs elevees.
Methode 2: Chiffres comparables, la methode est tres legere-ment plus sensible.

Materiel : Methode 1: Potentiographe avec polariseur. Electrode d'argent ou de platine (double) amalgamees.
Methode 2: (en plus de methode 1) conductiscope.

Produits : Ethanolamine . EGTA . NaOH . EDTA . Acide nitrique .
 Mercure . Nitrate de mercure . KCN .

Mots Cles: CALCIUM / MAGNESIUM / ELEC / VOLUM /

JRET

Authors : GREYER (C) - BRUTEL (P) & MAUSLI (F)
Title : The biamperometric determination of Potassium and/or Ammonium.
Public : Application Bulletin No. 100 e, Metrohm 1975.
Pages/ref: 2 pages

Summary

Potassium ion is precipitated with sodium tetraphenylborate added in excess. Excess reagent is back titrated with 0.02M thallium nitrate. The reaction is followed by a polarized double platinum electrode. This method is valid for potassium alone or in the presence of sodium and magnesium .

Ammonium may be determined as the difference ($(K+NH_4)-K$).

Potassium in the presence of calcium may be determined if a large excess of NaOH is added to the sample so that $Ca(OH)_2$ is precipitated quantitatively.

Precision: The titration is unaffected by chloride, Nitrate, Sulfate, Phosphate and Acetate anions.

Material : Potentiometric recorder connected to automatic burette - Polarizer - Double platinum electrode.

Chemicals: KCL ; Sodium tetraphenylborate ; NaOH ; HCL.

Key Words: POTASSIUM / NH_4 / ELEC /

Auteurs : GREYER (C) & BRUTEL (P)
Titre : Détermination potentiométrique des ions calcium et hydroxyde en solution aqueuse.
Public : Application Bulletin No. 81 f, Metrohm 1971.
Pages/ref: 2 pages / 2 ref.

Résumé:

On ajoute à l'échantillon un excès d'acide éthylène-glycol tétraacétique (EGTA) 0.1M dans NaOH 32% ajusté à pH 11.0. On titre en retour à l'aide de HCL N/5. La courbe de variation du potentiel en fonction du volume de HCL ajouté présente trois points d'inflexion qui correspondent le premier à l'ion OH, le second à l'excès de EGTA, et le troisième au complexe EGTA calcium.

Precision: -Le magnesium n'interfère pas dans la mesure.
-On peut doser de 10 à 250 mg/l de Ca pour un échantillon de 50 ml (soit 0.5 à 12 meq/l de Ca); la limite de detection est 2 mgr/l Ca.

Matériel : Enregistreur potentiométrique ; Burette automatique asservie au potentiomètre ; Electrode de verre.

Produits : HCL ; EGTA ; NaOH.

Mots Clés: CALCIUM / ELEC / SALINITE /

Auteurs : GRETHER (C) - BRUTEL (P) & HADINGER (O)
Titre : Determination potentiométrique de la dureté totale et de la dureté calcique au moyen d'une electrode ionique spécifique.
Public : Application Bulletin No. 101f, Metrohm 1975.
Pages/ref: 2 pages / 4 ref.

Résumé:

Une méthode très précise pour la mesure de la dureté de l'eau est présentée. A 100 ml d'échantillon d'eau, on ajoute 10 ml EDTA (Na)₂ 0.05 M. L'excès d'EDTA est titré en retour par une solution de sulfate de cuivre 0.05 M. La réaction est suivie à l'aide d'une electrode indicatrice du cuivre, et d'une electrode de référence au calomel.

La dureté calcique est obtenue de la même manière mais en complexant le calcium avec EGTA 0.05 M.

Precision: L'écart type relatif varie pour 40 échantillons de 0.3 à 0.6%.

Matériel : 1 enregistreur potentiométrique. 1 burette automatique asservie au potentiomètre. 1 electrode spécifique Cu. 1 electrode de référence au calomel.

Produits : EDTA ; EGTA ; CuSO₄ ; NH₄OH ; H₂SO₄.

Mots Clés: CALCIUM / MAGNESIUM / ELEC / CU /

Author : GRIFFIN (G.F)
 Title : Automated determination of Magnesium in soil extracts by Atomic Absorption Spectrometry.
 Public : Soil Sci. Soc. Amer. Proc. Vol. 32-1968.
 Pages/ref: 803-805 / 5 ref.

Summary

A procedure for determination of Mg by automated AAS is described. The sample is diluted in a peristaltic pump and fed into the spectrophotometer by a "well" device specially built for this purpose. The flow rates of the manifold used to dilute the sample are as follows:

Sample (0.32) / Diluent (3.90) / Air (1.20) / Double mixing coil / Waste (4.62) / Resampler (0.8) / Diluent (2.90) / Air (0.8) / Double mixing coil / Debubber / Waste (1.10) / Resampler (3.40) / Well specially designed / AA Spectrophotometer.

Magnesium is extracted from soils by shaking 4 gr of soil with 20 ml $(\text{NH}_4\text{OH} - \text{CH}_3\text{COOH})$ PH4.8 for 15 min.

Chemical interferences of Si, Al and P are studied. 100 ppm Al causes a slight reduction of the absorbance, suppressed by 1500 ppm Sr. Silicate does produce significant interference only when Ca is absent from the solution.

Tables : -- Flow diagram.
 -- Drawing of well device through which spectrophotometer picks up the sample from the manifold.
 -- Analysis of variance for two levels of Mg with different levels of Al, P, Si with and without 1500 ppm Sr.
 -- Comparison with manual procedure.

Precision: r.s.d is 2% at 10 ppm Mg level for sampling time greater than 60 sec. Precision decreases if the sampling time is reduced.

Key Words: MAGNESIUM / AUTOANALYSE /

Author : HESSE (P.R)
 Title : Water - soluble calcium and magnesium. In "methods of soil analysis"
 Public : Euphrate Pilot Irrigation project, Raqqa 1974.
 Pages : 2 pages.

Summary:

Soluble calcium and magnesium in 1/5 soil/water extract. Titration by EDTA of calcium and calcium + magnesium. Mg found by difference.

Method: Calcium

Shake 20 gr soil with 100 ml distilled water, 30 min. Filter or centrifuge. To 10 ml aliquot add 10 drops potassium cyanide 1%, 10 drops. Hydroxylamine - HCL 5%. 20 drops triethanolamine (pure). Add 2,5 ml sodium hydroxyde solution 10%, 1 ml solochrome dark blue (0.1% in methanol or ethanol) titrate with EDTA. Until blue EDTA should be standardized against standard Ca solution. A blank made with distilled water instead of Ca will help to visualize end point.

Calcium + Magnesium

To 10 ml aliquot add 15 ml buffer (6,75% amonium chloride in 57% concentrated (d=0.38) amonia, 10 drops KCN, 10 drops hydroxylamine - HCL, 10 drops K - hexacyanoferrate (II), 20 drops triethanolamine, 10 drops eriochrome black T titrate to blue end point.

Tables : No

Precision: Not given

Chemicals: Calcium carbonate . EDTA . NaOH . Amonium chloride . Hydroxylamine hydrochloride . Potassium hexacyanoferrate . Potassium cyanide . Triethanolamine . Solochrome dark blue . Eriochrome black T . Methanol (or ethanol) .

Key words: CALCIUM / MAGNESIUM / WATER / VOLUMETRY /

HESS

Authors : KARMIE GALLE (O)
Title : The determination of calcium and magnesium in carbon and silicate rocks.
Public : Annual Rocky Mountain Conference on Spectroscopy 1966.
Pages : 3 pages.

Summary:

Atomic absorption of calcium and magnesium in hydrogen/air flame after precipitation of R_2O_3 metal with ammonium hydroxide.

Interference of silica is eliminated in preparation step by HF treatment. The effect of acid nature and concentration is investigated, perchloric and hydrochloric acid showing the greatest sensitivity, this effect is more sensible on Ca than on Mg absorption. Interference of nitrate were eliminated by 1500 ppm strontium (as chloride) or ammonium chloride (1000 ppm). The effect of nitrate is not felt in air/acetylene flame.

Tables :- Schematic diagram of the method of sample preparation.
- Comparison of curves of calcium made up from different acids (1 to 25 ppm).
- Effect of different acids on magnesium (0 to 3.0 ppm).
- Comparison of AAS values with certified standard samples.

Precision: Range 1 to 25 ppm Ca at 422,7 nm.
0.1 to 3 ppm Mg at 285,3 nm.
Best precision is obtained for rocks containing 13 to 40% of calcium or magnesium.
Results show greater dispersion at 0.1 to 2% Ca or Mg level (60% for 6 determinations).

Material :- AA Spectrophotometer . Hydrogen supply . Calcium, Magnesium Hollow Cathod Lamp.

Chemicals: HF . HCL . $HClO_4$. Amonium hydroxyde . Amonium chloride .

Key words: CALCIUM / MAGNESIUM / CALC. CARBONATE /AAS/

KARM

Author : KITTRICK (J.M)
 Title : The separation factor applied to some soil ion exchange equilibria.
 Public : Soil Science Society of America Journal 49-1976.
 Pages/ref: 147-148 / 6 ref.

Summary:

The use of the separation factor $\alpha = C_A c_b / C_B c_a$ (1) where c and C are concentrations in soil solution (mL^{-1}) and in soil ($\text{eq}^{\text{K-1}}$) respectively is investigated. For montmorillonite data from others authors (cf. table 1) agreed well with equation (1). Data for 198 samples of arid zones calculated for Na and Ca (c =concentrations in saturation extracts and C values of exchangeable Na and (Ca+Mg) respectively, exchangeable Ca being calculated as CEC - exchangeable sodium - exchangeable potassium) resulted in equation (2).

$$\log C_{\text{Na}} / C_{\text{Ca}} = 0.79 \log a_{\text{Na}} / a_{\text{Ca}} - 1.41 \quad (2)$$

where a stands for activities in saturation extract. Author notes that there is some question as to whether the ionic activities in the saturation extract are in equilibrium with exchangeable ions. The intercept - 1.41 cannot be considered to be the logarithm of the separation factor because the slope of eq. (2) is not equal to 1.

Tables : - exchange data of Vanselow (1932) and Eliason (1966) for montmorillonite plotted according to eq. (1).

Precision: $r=0.98$ between $\log a_{\text{Na}} / a_{\text{Ca}}$ in saturation extract and $\log C_{\text{Na}} / C_{\text{Ca}}$ of exchange sites (NH_4OAC extraction) for 198 soils of arid zones.

Key Words: CEC / Na-LABIL / Ca-LABIL / SALINITY /

KITTR

Auteurs : KREMPF (G) & MILLION (D)
Titre : Dosage du Calcium et du Magnesium.
Public : Methodes de dosage utilisees au Centre de Sedimentologie.
University Louis Pasteur, Strasbourg.
Pages : 33 - 36 .

Resume:

Dosage du calcium et du magnesium par absorption atomique avec utilisation d'une pompe proportionnante pour preparer les solutions.

Le diagramme est le suivant: Echantillon (2 x 2.0)/ Tampon A ou B (0.42)/ Double bobine / Spectrophotometre.

- Le tampon d'ionisation A, utilise pour le calcium est une solution a 13.4 gr/l de chlorure de cesium (ou 11.2 gr/l d'oxyde de cesium meilleur marche).
- Le tampon spectral pour Mg est une solution a 118gr d'oxyde de lanthane dissous dans 300 ml d'HCL concentre et ramene a 1 litre.

Les longueurs - d'onde sont 422.7 (Ca) et 285.2 (Mg).

Figures :- Diagramme de flux continu.
- Courbe concentration / precision.

Precision: Pour Ca, l'ecart type relatif est: 10% a 0.020 meq/l.
2.5% entre 0.2 et 1 meq/l.
Pour Mg, l'ecart type relatif est: 10% a 0.020 meq/l.
5% a 0.06 meq/l.
1% entre 0.1 et 0.2 meq/l.

Materiel : Spectrophotometre AA . Pompe proportionnante 5 canaux .
Echantillonneur.

Produits : Oxyde de lanthane . Oxyde de cesium .

Mots Cles: CALCIUM / MAGNESIUM / EAUX / AAS /

KREM

Authors : LEE (R) & GIBSON (E. JANICE)
 Title : Magnesium in New-Zealand soils: IV. Determination of non exchangeable magnesium using a cation exchange resin.
 Public : New Zealand J. of Agric. Research 19 - 1976.
 Pages/ref: 63-68 / 16 ref.

Summary:

A method is proposed to analyse a large number of samples for non exchangeable Mg when the quantity of Mg is less than 40 meq/100 gr of soil. Principle is an extraction with cation exchange resin, (exchangeable Mg is subtracted). The result provides potentially plant available non exchangeable Mg. The method was described in a previous paper it uses 5 gr soil and 8 grams 20-50 mesh H-resin. Exchangeable Mg is determined in N neutral amonium acetate and total Mg by nitric hydrochloric digestion, with evaporation of Silica.

Tables :- Analysis of variance of the reproductibility of the resin method.. (4 replicates , 12 soils from 1.5 to 110 meq/100g Mg).
 - Regression analysis of resin-Mg on total-Mg. ($r = 0.92$ range is 0-300 meq/gr); regression of resin-Mg on reserve-Mg, and regression of reserve-Mg on total-Mg.
 - Effect of varying amounts of resin and time of shaking on resin-Mg values (four soils, 2 to 16 gr of resin are used, shaking time is 16.20 and 24 hours).

Precision: A significant difference between runs is found which does not appear in "within-run" variation showing the importance of experimental condition control (temperature).

Chemicals: Amonium acetate . H-resin 20-50 mesh .

Key Words: MAGNESIUM / RESIN /

Authors : NEMETH (K) & GRIMME (H)
 Title : Effect of soil PH on the relationship between K concentration
 in the saturation extract and K saturation of soils.
 Public : Soil Science 114-5-1972.
 Pages/ref: 349-354 / 15 ref.

Summary

An investigation to find out a quantitative relationship between K saturation of inorganic CEC, K concentration in saturation extract and PH is presented. The soils studied are Podzols (0.2-0.5% O.M) and Chernozems (4-5% O.M) having a pH (0.1N KCl) varying from 3.1 to 6.7 and a clay percentage 20% \pm 3. The soils were artificially saturated in K up to 10%. Illite was the main clay constituent of the soils studied.

Method: Exchangeable K was determined by percolation with NH_4OAc N; To determine CEC, the soil was saturated with $\text{BaCl}_2 \cdot 0.2\text{N}$ buffered by triethanolamine at pH 8.1. Effective CEC is done with the same unbuffered reagent. The washing step is done by 0.02N Ba and excess Ba is estimated by weighting. Displacement step is done by Mg.

The organic CEC is measured after destruction of the organic water with H_2O_2 .

The inorganic CEC decreased with decreasing pH of the soil for horizon B of the Chernozems. At a given saturation, the concentration of potassium in the saturation extract increases as pH decrease (Podzolic soil) indicating a less strong bonding of K explained by the competition from Al.

Tables : - Properties of the soils.
 - Relationship between K saturation % and K in sat. extract at different pH. Regression equations, (for saturation percentage of inorganic CEC and total CEC).

Key Words: POTASSIUM / SALINITY / PH / ECEC /

Author : xxx / ORION
 Title : Divalent cation activity electrode, model 92 - 32.
 Calcium ion activity electrode, model 92 - 20.
 Public : ORION Research Incorporation 1967.
 Pages : (4 p + 4 p).

Summary:

Electrode responding to divalent cation may be used to determine water hardness and end point titration in EDTA titrations. The electrode is calibrated in standardized solutions of known activity or known concentration at constant ionic strength.

Tables : First Publication

- Typical potential electrode versus calcium ion activity and calcium chloride concentration, (range 0.1 to 1000 millimoles/l, also printed in the second publication).
- Electrode potential behavior versus solution PH. (PH 2 to 11) for magnesium and calcium chloride at different concentrations.
- Approximate divalent cation selectivity constants (PH 6) for Zn, Fe, Cu, Ni, Ba, Sr (based on Ca, Mg=1,00).

Second Publication

- Divalent cation selectivity table (Ca 1,00): Zn⁺⁺, Fe, Pb, Cu, Ni, Sr, Mg (Mg = 0.014) Ba.
- Electrode potential behavior versus solution PH (pure calcium chloride solutions 0.1 to 1000 millimoles Ca/l).

Material : Divalent selective electrode - Calcium ion selective electrode - PH-ionmeter .

Chemicals: Calcium activity standard . Water hardness activity standard .

Key Words: CALCIUM / MAGNESIUM / ELEC / VOLUMETRY /

ORIO

Authors : OSTER (J.D) & SHAINBERG (I)
 Title : Exchangeable cation hydrolysis and soil weathering as affected by exchangeable sodium.
 Public : Soil Science Society of America Journal 43-(1)-1979.

Summary:

Exchangeable and cristalline cations are released from soil minerals as a result of hydrolysis and weathering. Rates of hydrolysis and the resultant changes in the cation exchange composition of three lime free arid zones soils as affected by different values of exchangeable Na are studied.

Methods: Lime was removed by 1N NaCl/HCL at constant pH4 to 5; (contact time 24 to 72 hours). Then soils were equilibrated with solutions having a S.A.R of 5,20 and "infinite" (prepared from chloride of Na, Mg, Ca). PH and Electric Conductivity were measured during the equilibration period (7 to 14 days). The initial CEC was measured by Na-NH₄OAC method and EC by NH₄OAC pH7.

Results: The conductance of aqueous suspensions when plotted versus the square root of time, exhibited two linear segments. Authors conclude that the release of Ca, Mg, K from silicate minerals is more rapid than the hydrolysis of exchangeable Na and Ca for the three soils considered. The removal of CaCO₃ was suspected to produce intermediate products controlling release of Ca, Mg, K. The rate of exchangeable Ca hydrolysis and release from silicate materials was sufficient to saturate the solution with respect to lime for the calcic haploxeralf soil.

Tables : - General properties of soils (CEC - CaCO₃ - Clay - Silt-clay minerals).
 - EC composition before and after the treatments.
 - Relation between specific conductance and time for equeous suspensions of three soils.
 - Total initial and final EC and changes in exchange ion composition.

Material : AA Spectrophotometer (for Ca, Mg, Na and K). Chloride titrimeter. Potentiometric titrator . (For carbonates and bicarbonates). Centrifuge.

Key Words: CEC / SALINITY / SODIUM / LABIL /

Authors : PEASLEE (D.E)
 Title : Colorimetric determination of Calcium in soil extracts.
 Public : Soil Science 4 - 97 - 1964.
 Pages/ref: (248 - 250 / 7 ref.)

Summary:

Microdetermination of calcium in soil extracts by spectrophotometry of the red complex formed at pH 12 with glyoxal-bis-(2 hydroxyanil), (referred to as GBH) at 535 nm. Application is studied from 0.05 to 5 ppm Ca. A macro-colorimetric and a spot test as well are proposed using the same reaction.

Micro method:

Aliquot containing 1 to 30 micrograms Ca adjust ionic strength and composition to those of extracting solutions, add 10 ml MEQH, 1.0 ml buffer (5.28 g/l sodium tetraborate in sodium hydroxide 1%) add 0.5 ml reagent (0.45% GBH in absolute MEQH), mix wait 25 minutes, measure absorbance at 535 nm versus blank. Appreciable interferences of phosphate, Ba, Sr, Fe, Cu, Mn are reported ; Addition of carbazone eliminate interferences of the last three elements. A ratio of 1/25 for P/Ca concentration in the extract is tolerated without interference.

The method is tested using (0.734M NaOAC + 0.528M HOAC) as extracting solution and ½ soil solution ration. Reference method choosed was calcium oxalate precipitation and subsequent titration of dissolved precipitate by K permanganate N/100.

Macro colorimetric test use a 50 microliters aliquot. Calcium is determined with the same reagents, with a relative error less than 8% in the 120 to 525 ppm range.

Tables : R.s.d is 0.6% for 1 sample at 1.61 ppm level on quadruplicate determinations.

Precision: Agreement of proposed method with standard is better than 3% in the range 0.1 to 3 ppm.

Material : Spectrophotometer - (1 cm cells) - Micropipette.

Chemicals: Calcium carbonate . Glyoxal-bis-(2 hydroxyanil). Ethanol . NaOH . Sodium tetraborate . Na diethyldithiocarbamate . Methanol .

Key words: CALCIUM / COLORIMETRY / SOL / LABIL /

PEAS

Auteur : PELLOUX (P)
 Titre : Methodes de determination des cations echangeables, de la capacite d'echange dans les sols courants calcaires ou non, mais ni sales, ni gypseux.
 Public : Service des Sols, ORSTOM 1963 .
 Pages/ref: 55 pages / 7 ref.

Resume:

Une methode permettant la determination de la capacite d'echange des sols peu calcaires utilisant le calcium comme ion saturant et le chlore comme ion traceur est decrite. Les risques d'hydrolyse sont evites en eliminant l'etape de lavage.

Methode:

Percoler 10 g de terre par 500 ml de chlorure de calcium tamponne a PH 7 par de la triethanolamine, puis par 150 ml de chlorure de calcium N/10. On deplace le calcium par 500 ml de nitrate de potassium N. On dose dans le percolat Ca et l'anion Cl qui permet d'evaluer l'excès de chlorure de calcium retenu par capillarite. On titre les carbonates et bicarbonates par acidimetrie pour connaitre la quantite de calcium dissoute par le reactif utilise. On peut egalement doser dans l'extrait au chlorure de calcium, le sodium et le potassium echangeable.

Le calcium est dose par colorimetrie en flux continu (BRION) par le montage:

(Echantillon (0.23) / Air (0.32) /) // (Tampon diethylamine (1.2) / Cresolphtaleine 0.05% dans HCL 0.25N (0.32) / Agitateur magnetique // Bobine melange 10 tours / Colorimetrie 15 mm , 570 nm .

Figures :- Schema de montage des colonnes de percolation.
 - Systeme de percolation automatique.

Produits : Chlorure de calcium . Triethanolamine . Nitrate de potassium . Helianthine acide chlorhydrique . Diethylamine . Gamme de potassium.

Mots Cles: EC - CEC / CALCIUM / AUTOANALYSE /

PELL

Authors : PERUR (N.G) - MITHYANTHA (M.S)
Title : Methods of measuring available potassium in soil.
Public : Bull. Ind. Soc. Soil Science 10, 1976.
Pages/ref: 299-305 / 29 ref.

Summary

The methods for determining available potassium are reviewed and their respective merits are briefly discussed. Chemical extractants are classified as empirical methods. The ammonium acetate 1N PH7 extraction is used as reference. A second type of method which is based more on theory of fixation of K on soils is also described. In this procedure the availability of potassium is determined by a number of factors:

- A quantity factor (Q), an intensity factor (I), a rate factor (R), a buffer capacity factor and a geometric factor (G).

From the point of view of plant growth, the intensity factor is the most important. The procedure of determination of Q-I relationship is outlined. The relationship between available potassium and plant response is discussed. An important drawback of chemical extraction is that it does not take into account the effect of others cations in soil. The physico-chemical methods involve many different factors and are not standardized. They are not applicable to routine work. Relationship of available potassium with soil properties is discussed with special reference to soils of India.

Key Word: POTASSIUM /

PERU

Auteur : QUANTIN (A)
Titre : Automation des dosages des principaux ions échangeables du sol.
Public : Fascicule de Botanique No. 3. Université de Besançon 1956.
Pages : 6 pages.

Resume:

Les principales méthodes de dosage en flux continu des cations échangeables sont passées en revue. Dans tous les cas, les dosages sont en milieu acetate amonium N. Pour Ca sont présentes. Colorimétrie à la murexide, photométrie de flamme en flamme propane - oxygene (2775°C) et fluorométrie à la calceine. La méthode murexide donne des résultats peu reproductibles. La fluorométrie se fait à 485 nm (excitation 405 nm).

Diagramme (ml / min):

Echantillon (0.16) / NaCl 0.9% (3 x 3,9) / air (1.2) / bobine double / calceine 0.004% dans NaOH 2,5% (2.5) / 2 x bobines doubles / fluorométrie / repompage (2,5) /
Lavage à l'acetate d'amonium entre chaque échantillon.

Figures : Diagrammes de flux continu (murexide, photomètre à flamme et fluorométrie).

Precision: Gamme de 0.1 à 7.5 meq/l de Ca pour fluorométrie.

Materiel : Pompe peristaltique multi-canaux, fluoromètre - (photomètre à flamme - colorimètre).

Produits : Acetate amonium . Calceine . Soude . Carbonate de calcium . Acide chlorhydrique . NaCl .

Mots Cles: CALCIUM / FLUOROMETRIE / SOL / ECHANGEABLE /

QUAN

Auteur : QUANTIN (A)
 Titre : Dosage du Magnesium échangeable.
 Public : Université de Besançon - Fascicule de Botanique No.3 - 1966.
 Pages/ref: 7-9

Résumé

L'auteur présente deux méthodes en flux continu pour le dosage du magnésium:

1. Une méthode colorimétrique utilisant le Jaune de titane à 550 nm qui permet le dosage de 1 à 5 meq/100 gr de Mg échangeable dans le sol. Le diagramme est le suivant:

Echant. (0.6) / Air (1.6) / H₂O (2.9) / Bobine simple / Débul-
 lage / Reprise (1.6) / Air (1.6) / Solution compensatrice
 (2.2) / Jaune de titane (1.6) / NaOH (2N)/.

2. Une méthode fluorimétrique utilisant le 8-hydroxyquino-
 léine dans l'éthanol. La fluorescence du Mg est activée par
 une lumière de 420 nm. Dans le montage décrit on utilise une
 excitation à 405 nm.

La fluorescence émise étant mesurée à 485 nm, le montage est
 le suivant:

Echant. (0.42) / Air (1.6) / Tris (0.6) / Bobine simple / Ethanol
 (3.9) / Bobine simple / Hydroxyquinoléine (2.5) / Bobine simple /
 Débullage / Reprise (2.9) / Fluoromètre/.

Produits : Méthode 1. Jaune de titane - Chlorhydrate d'hydroxylamine -
 EGTA - NaOH - HCN - Chlorure d'aluminium - KCN -
 Alcool polyvinylique.

Méthode 2. Tris - Hydroxyquinoléine - Méthanol - Acetate -
 d'ammonium - Ethanol.

Key Words: MAGNESIUM / COLORIMETRIE AUTOMATIQUE / FLUOROMETRIE /

Author : QUEMENER (J)
 Title : The measurement of soil potassium.
 Public : IPI Research Topics No.4 - Beru 1979.
 Pages/ref: 1-48 / 101 ref.

Summary

The first part of this comprehensive study on potassium in soils describes the forms of potassium in soils: Exchangeable Potassium, Reserve Potassium, Potassium in Soil Solution. A large place is devoted to theory.

The second part describes the analytical techniques used to measure all the parameters which give a complete picture of potassium, namely:

- Exchangeable potassium, potassium in soil solution, release from reserves, fixation on interlayer sites and mobility for each type of potassium the literature is surveyed and prominent methods are briefly described.

Part III describes a practical soil analysis policy and interpretation of results for fertilizer advice.

- Tables :
- Possible forms of potassium in soils (diagram).
 - Example of a curve describing the quantity relationship of a soil.
 - Relationship between K uptake and exch. K in Stanford's microculture.
 - Effect of drying soil samples on balance of K exchange.
 - Examples of K extracted from soils by various salt solutions on amphibolite; examples of exchange isothermes for several soils from Champagne.
 - Picture showing extraction of soil potassium by Stanford de Ment's method.
 - Successive extraction of K from soil by HNO_3 N after removal of exchangeable K.
 - Relationship between K uptake and amount of K extracted by various chemical reagents.
 - Total K balance as related to change in exch. K and NaTPB extracted K.
 - Study of potassium diffusion using discs of resin-impregnated paper in contact with soil.
 - Relationship between K concentration of the sat. extract and % K saturation of soil; and between diffusive flux.
 - Electro-Ultra-filtration equipment, principle and desorption curves.
 - Example of diagrams giving soil K availability in relation to a) clay content and clay saturation. b) K saturation and CEC.
 - Showing interrelationship between K saturation K release and response to fertilizer-K by cereals.

Key Word : POTASSIUM /

QUEM

Authors : RICE (H.B) & KAMPRATH (E.J)
Title : Availability of exchangeable and non-exchangeable Mg in sandy coastal plain soils.
Public : Soil Sc. Soc. Am. Proc. Vol 32-1968.

Summary

The paper studies the release of non-exchangeable Mg by chemical extraction and plant uptake. This release was found to be the highest for soils containing expansible clay minerals (as measured by the ethylene glycol method). The soils studied were sandy soils with clay content of 3 to 10% and CEC lower than 4 meq/100 gr. The CEC of soils was determined by neutral NH_4OAc . Exchangeable Mg was extracted by shaking 10 gr of soil with 50 ml NaCl 0.1N for 30 min. twice. To estimate the proportion of non exchangeable Mg two extractions were made. The first with 1N, PH7 NaOAc was suppose to contain only exchangeable Mg while the second made with 1N, PH 1.0 NaOAc was suppose to contain exchangeable plus some non-exchangeable magnesium.

- Tables : - Soil properties and estimated clay mineral in the Coastal Plain Soils (5 soils).
- Exchangeable and total Mg content of soils studies.
- Mg released by 1N, NaOAc solution at PH1 and PH7.
- Plant uptake of Mg from exchangeable and non-exchangeable sources.
- Mg uptake by corn as related to the initial Mg content.

Key Word : MAGNESIUM /

Authors : SCHULZ (R.K) - OVERSTREET (R) & BARSHAD (I)
 Title : Some unusual ionic exchange properties of sodium in certain salt-affected soils.
 Public : Soil Science 99-3-1964.
 Pages/ref: 161-165 / 7 ref.

Summary:

For some soils containing zeolitic minerals, the authors propose to consider as acceptable exchangeable sodium the sodium removed from the soil by exchange for Ca^{++} ion. In their experiment, a soil sample was equilibrated with Na22 and then labeled-samples were extracted by CaCl_2 , NaCl_2 , NaCl, KCl, NH_4OAc and HCl solutions. Na22 remaining fixed on exchange sites of soils was minimum after NaCl extraction (0.3meq / 100gr for an initial value of 20.5meq/100gr), and maximum after CaCl_2 extraction. This unusual behavior led to an x-ray diffraction study of clay material which revealed part from 35% illite, 15% montmorillonite, some 35% of analcime, or $\text{NaAl}(\text{SiO}_3)_2 \cdot \text{H}_2\text{O}$. This zeolitic mineral may be responsible of the fixation of sodium in such a way that it may be removed more easily by K^+ or NH_4^+ than by Ca^{++} .

Tables : - Exchangeable Na content of soil determination by isotopic dilution experiments.
 - Effect of various extractants on Na22 labeled soil.
 - Diagnostic x-ray spacings for the identification of analcime.

Material : Radioisotope counter.

Chemicals used: NH_4OAc - CaCl_2 - KCl - Na22 .

Key Words: EXCH. Na / X-RAY / RADIO / SALINITY /

Author : S.C.S
 Title : Chemical Analysis - Magnesium - pg. 45
 Public : Soil Survey Laboratory Methods and procedure for collecting
 soil samples, SSI Report No.1 .
 Pages/ref: 45-47 / 3 ref.

Summary:

Six different procedures for total or exchangeable magnesium are presented:

1. Mg in saturation extract by EDTA titration using Eriochrome Black T as indicator.
2. Mg in NH_4OAc extract by the same method after evaporation of $\text{Mg NH}_4\text{OAc}$ - alcoholic solution.
3. Precipitation with Diammonium hydrogen phosphate, dissolution of the precipitate by H_2SO_4 and backtitration with NaOH . Alternative: by gravimetry of $\text{Mg}_2\text{P}_2\text{O}_7$ precipitate.
4. From KCl -triethanolamine extracts and EDTA titration.

Chemicals: 1. EDTA titration: NH_4OH - NH_4Cl /EDTA/
 Hydroxylamine hydrochloride - Mg-verseinate (EDTA-Mg-Na_2)-
 Eriochrome Black T.

2. Phosphate titration: NaOH - H_2SO_4 / NH_4OH /
 Diammonium hydrogen phosphate - Bromocresol green -
 hydrochloric acid.

Key Words: MAGNESIUM / TITRIMETRY / GRAVIMETRY /

Author : xxx / Soil Survey
Title : Calcium by oxalate precipitation
Public : Soil Survey Laboratory methods and procedures for
collecting soil samples 1972.
Pages/ref: 42 - 43 / 2 ref.

Summary:

Determination of calcium in amonium acetate (N PH 7) extracts (cation exchange capacity or exchangeable basin) by precipitation at PH 4.6 as calcium oxalate, dissolution in concentrated sulfuric acid and titration by potassium permanganate. An alternative procedure is proposed when aluminium, iron and/or manganese are present.

Method:

Aliquot of amonium acetate extract is evaporated to dryness, dissolved nitric/hydrochloric acid (10/2 ml), dry again. Residue is heated up to $390^{\circ} \pm 10^{\circ}\text{C}$ twenty minutes. Silica is insolubilized by 3 ml HCL 6N twice to dryness. 5 ml oxalic acid is added, boiled, PH adjusted to 4.6 by amonia/N (bromocresol green indicator). Boil one hour 80°C . Collect precipitate, wash with saturated oxalate - solution dissolve in hot sulfuric acid (conc) titrate by standard potassium permanganate.

Chemicals: Oxalic acid . Bromocresol green . Amonium hydroxide .
Sulfuric acid . Potassium permanganate . Calcium
oxalate .

Key Words: CALCIUM / VOLUMETRY /

SOIL

Auteurs : SUSINI (J) & ROUAULT
 Titre : Utilisation d'une electrode spécifique pour le dosage du sodium dans les eaux et les extraits de sol.
 Public : Cah. ORSTOM Pedo. Vol.X, No.3-1972.
 Pages/ref: 12 pages / 8 ref.

Résumé:

L'article commence par un bref rappel théorique sur le fonctionnement des electrodes ioniques spécifiques et des interférences à craindre. L'appareillage pour le dosage du sodium est décrit en détail. La pente moyenne de la courbe d'étalonnage est de 59mV avec l'appareillage utilisé.

L'effet de la température est étudié et une variation de $\pm 5^{\circ}\text{C}$ produit une erreur décroissant de 20% pour 1ppm Na à 7,5% pour 10^3ppm (l'erreur est négligeable au niveau de 10^4ppm de Na).

L'influence du pH et des anions Cl^- , CO_3^- , SO_4^- est étudié à un pH constant de 10 obtenu par barbotage d'amoniac.

L'effet du gypse est étudié également, l'interférence n'existe que pour Na inférieur à 3ppm, ce qui est une valeur rare dans les extraits de sols gypseux. L'utilisation de l'electrode spécifique à la mesure du sodium dans les extraits de sol et les eaux salées est comparée avec la photométrie de flamme.

Figures : - Etalonnage de l'electrode (-160 à +110mV).
 - Variation de pente avec la température pour des concentrations de 1 à 10^4ppm Na.
 - Variation absolue en mV suivant le pH (pH=5 à pH=10).
 - Interférences des sulfates, carbonates, gypse.
 - Etendues des mesures: de 23.000 à 0.23 mgr/l en Na (soit pNa 0 à 5).

Précision: - L'écart-type calculé sur 10 mesures ne dépasse pas 3mV de 1 à $5 \cdot 10^4\text{ppm}$ en Na.
 - Pour des eaux de pH compris entre 7.7 et 8.4 l'erreur relative par rapport à la mesure en spectrophotométric de flamme est:
 - 1% au niveau de 100ppm Na
 - 2% au niveau de 400ppm Na
 - de 4 à 8% pour des valeurs inférieurs à 60ppm Na.

Mots Clés: SODIUM / SALINITE / GYPSE /

SUSI

Authors : SWANSON (R.A) - HOVLAND (D) & FINE (L.O)
Title : Fluorometric determination of Magnesium in soil extracts.
Public : Soil Science 102-4-1966.
Pages/ref: 244-247 / 8 ref.

Summary

Some azo compounds are known to form Ca and Mg derivatives emitting a fluorescence which can be used in analysis. Such a compound is O-O'-dihydroxy-azobenzene. Authors study the interference of foreign ions by artificial solutions of Al, PO_4 , Na, SO_4 , Cl... simulating soil extracts. Interference of Ca is studied with Ca/Mg ratio varying from 1/30 to 1/2 and partially overcome by adding a Ca buffering solution to standard and samples. Recovery of Mg added to saturation extracts of soils containing 5 to 23 ppm Mg was within 10% (in the range of 5 to 10 ppm Mg added).

Fluorometric analysis is compared to AAS and Thiazol yellow colorometry in ammonium acetate and saturation extracts of soils. The fluorometric analysis was found as reliable as AAS for the 8 soil samples.

Tables : - Effect of added Ca on the Mg found using two different working solutions to develop the fluorescence.
- Recovery of Mg added to saturation extracts.
- Comparison of fluorometric analysis with atomic absorption and thiazol yellow colorimetry.

Chemicals: O-O'-dihydroxy-azobenzene / Ethanol / Ethylenediamine / HCL / Triethanolamine / $CaCO_3$ / Mg standard /
Thiazol yellow method: reagents are not given.

Key Words: MAGNESIUM / COLOR /

Author : SYTNIIEWSKI (A)
 Title : Determination of sodium in concentrated saline by flame photometry.
 Public : Chemia Analityczna 21 - 245 - 1976.

Summary

The method was developed to analyse sodium in brines having as much as 109 to 127 gr/l (i.e 4700 to 5500 meq/l) sodium as sodium chloride.

Method: 0.125 or 0.250 ml of brine is sampled by a syringe-micropipet and diluted 1/1000 to 1/4000. A standard curve was prepared from an artificial brine having a similar composition in salt with respect to calcium Magnesium, Chloride and Sulphates.

The measurement is made in two steps, in the first one the approximate concentration of the diluted solution is estimated on one calibration curve and then the sample is measured between two standard solutions of neighbouring values. Reproducibility is about 1%.

Tables : - Calibration curves in the range:

4 to 40 mgr/l Na
 54 to 64 mgr/l
 105 to 130 mgr/l

- Exemple of two steps determination for 30.1 - 30.8 - 31.3 mgr/l Na by the proposed method.

Precision: The average result of photometric determination on artificial brines agreed within 1% with known sodium concentrations.

Material : Flame Photometer.

Key Words: SODIUM / SALINITY /

Authors : TOMSON (M.B) , BARONE (J.P) & NANCOLLAS (H)
Title : Precise calcium phosphate determination.
Public : Atomic Absorption Newsletters 5 - 16 - 1977.
Pages/ref: 117 - 118 / (5 ref.)

Summary:

Calcium and phosphate are determined in the same solution using an AA Spectrophotometer with a Ca hollow cathod lamp as a light source for AA of Ca (422,7 nm) and molecular absorption of phosphate (maximum at 420 nm). The method is said to be more precise than conventional separate calcium and phosphorus determination for assessing calcium phosphate concentrations.

Calcium chloride solution were prepared from calcium carbonate and HCL, passed through H - cation resin and concentration checked by acid titration.

Tables : Absorbance of calcium and phosphate mixed solutions and corresponding relative standard deviation from 0.1 to 1 meq/l varies between 0.16 and 0.37% .

Precision: Careful C₂H₂ pressure regulation is recommended to avoid flame noise in Ca determination.

Material : AA Spectrophotometer - Adapted 1 cm quartz cell.

Chemicals: Lanthanum oxyde . Calcium carbonate . Amonium molybdate . Amonium vanadate . Potassium dihydrogen phosphate .

Key words: CALCIUM / PHOSPHORUS / AAS -- METHODS /

TOMS

Author : VERIGINA (K.V)
 Title : A comparison of methods of determining exchangeable calcium and magnesium in calcareous and gypsiferous soils.
 Public : Soviet Soil Science 1964.
 Pages/ref: 969-976 / 12 ref.

Summary:

Four methods are compared:

Method (a) Relies on NaCl solution to leach out exchangeable calcium and exchangeable magnesium. Correction is made for soluble Ca assuming that calcium carbonate dissolution is proportional to the volume of leaching solution. Method (b) uses also a NaCl solution but the amount of calcium carbonate dissolved is estimated by measuring the alkalinity of the filtrate. Method (c) Uses a single 3N NaCl treatment. Method (d) uses a mixture of ammonium, acetate oxalate, carbonate which is said not to dissolve any carbonate.

For gypsic soils, two methods (e) & (f) are compared: in method (e) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is changed into calcium carbonate by treating the soil (10 gr), with barium (1 gr), and then as proposed in methods (a) to (d). In method (f) soil is treated with an alcoholic solution of sodium sulfate in which neither calcium carbonate nor gypsum are dissolved. Exchangeable calcium is precipitated as CaSO_4 and estimated from the decrease in SO_4 concentration.

After having tested all the methods, the author concludes that method (a) gives results too low by 10-15%, method (b) is not applicable to dolomite soils, but is convenient for calcareous soils, in method (e) calcium carbonate is dissolved, method (d) gives only exchangeable calcium, method (e) gives good results providing the soil is shaken with barium carbonate during 24 hours, method (f) underestimates exchangeable Ca.

Tables : - A comparison of values of adsorption capacity and methods (a), (b) & (c) on chernozem and Sierozem (three tables).
 - Solubility of calcium carbonate in NaCl, CaCl_2 mixtures (two tables).
 - Effect of time of reaction of CaSO_4 with BaCO_3 on completeness of reaction.

Chemicals: Sodium chloride - Ethanol - Calcium chloride - Ammonium carbonate - Ammonium oxalate - Barium carbonate - Sodium sulfate.

Key Words: GYPSUM / CEC /

Authors : WARD (D.A) & BICHLER (D.G)
Title : Rapid, direct determination of calcium in natural waters by
Atomic Absorption Spectrometry.
Public : Atomic Absorption Newsletters 1 - 14 - 1975.
Pages/ref: 29 - 31 / 3 ref.

Summary:

A sodium ionization suppressant was studied for calcium determination by AAS at 422,7 nm in nitrous oxide/acetylene stoichiometric flame for water containing 0.05 to 200 ppm sodium ion. The enhancement of calcium absorbance due to ionization suppression is reached at level 500 - 2000 ppm added Na.

Aluminium at concentrations greater than 100 ppm produced a negative interference even when Na ion suppressant was used. The same was true for silicon whereas phosphates and sulfate did not produce any interferences.

A 1/2 sample dilutor is used to dilute sample with the 2000 ppm Na solution. A capillary T is described.

Tables :- Photograph of capillary diluting device.
- Graph of absorbance of 50 ppm Ca versus Na concentration.
- Influence of Fe, Zn, Mg, K, Al on 50 ppm Ca solutions in N₂O / C₂H₂ flame.
- Influence of sulfate and phosphate ions on solutions when aspirated with 2000 ppm Na.

Precision: Comparison of EDTA titration with AAS used with Na suppressant on eleven results of Ca in natural water from 70 to 120 ppm Ca, a difference of less than 2% between the two methods.

Material : AA Spectrometer - Capillary plastic tube.

Chemicals: Calcium standard. Sodium chloride .

Key words: CALCIUM / AAS - PRECISION / WATER /

WARD

Authors : WELLS (C.G) & COREY (R.B)
Title : Elimination of interference by phosphorus and other elements
in the flame photometric determination of Calcium and Magnesium
in plant tissue.
Public : Soil Science Soc. of Am. Proc. 1960.
Pages/ref: 189-191 / 9 ref.

Summary

A procedure for elimination of P, Fe, Al and K interferences in the determination of Ca and Mg in plant tissue using flame photometer was devised.

Method: The sample is ashed and dissolved in 10 ml of a 4N HCL solution containing 5 of FeCl_3 and 10g/l KcL. PH is adjusted to 5.6 by NH_4OH , then volume is completed to 100 ml with distilled water while NH_4OAc is added to prevent the burner to be clogged with NH_4Cl . This procedure precipitates all of P, Fe and Al without significant coprecipitation of Mg and Ca. After filtration Ca and Mg are determined by flame photometry at 422.7 nm for Ca and 285.2 nm for Mg using Air/acetylene flame.

Addition of 500 ppm K and 5 ppm Na to both sample and standard is useful to eliminate K and Na interference.

Tables : - Effect of K concentration on Ca in 0.4N HcL and in a solution
0.4N with respect to both NH_4OAc and NH_4Cl .
- Effect of P removal on the accuracy of the Ca determination.
- Effect of P removal on the accuracy of the Mg determination.

Material : Flame Photometer.

Chemicals: HcL ; FeCl_3 ; KcL ; NH_4OH ; NH_4OAc .

Key Words: CALCIUM / ASPECT / MAGNESIUM /

Auteur : WOLF (S)
Titre : Determination de la teneur en Ca et Mg par un titrage photometrique automatique en prenant comme exemple l'analyse du ciment.
Public : Metrohm - bulletin No. 22 f.
Pages : 2 pages

Resume:

Ca et Mg sont determines par complexometrie avec determination photometrique de la fin de reaction en utilisant en potentiographe relie a un colorimetre a 620 nm.

Methode: Calcium

50 ml aliquote, ajouter NaOH 2N jusqu'a PH 12,5 (PH-metre), 1 pincee murexide (1% dans NaCl solide), placer le recipient de titrage dans le colorimetre et titrer en enregistrant la courbe d'apbsorption.

Calcium + Magnesium

50 ml aliquote, ajouter 10 ml tampon PH10 (chlorure d'amonium a 5,4% dans amoniaque concentre, dilue a 35%). La triethanolamine est utilisee seulement en presence de Fe, Ti, Al et Mn.

La methode photometrique est meilleure que la methode potentiometrique (avec electrode indicatrice a cupule au mercure) lorsqu'on emploie le complexant triethanolamine.

Materiel : Potentiographe . Colorimetre . Equipement de titration automatique . PH metre . Electrode de verre .

Produits : Murexide . EDTA . NaOH . Triethanolamine . Chlorure d'amonium . Amoniaque .

Mots cles: CALCIUM / ELEC / EAUX /

WOLF