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CHEMICAL ANALYSES ON SOIL MATERIAL AND SOIL MOISTURE

Laboratory methods used during "Research on Acid Sulphate Soils in the Humid Tropics", Wageningen

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SCIENTIFIC REPORT
NO 8

RESEARCH ON ACID SULPHATE SOILS IN THE HUMID TROPICS

CHEMICAL ANALYSES ON SOIL MATERIAL AND SOIL MOISTURE

(Laboratory methods used in Wageningen)

modeling component

P. Bouter and C. J. Ritsema

SUPPORTING MINISTRIES

Ministry of Agriculture, Indonesia
Ministry of Agriculture and Fisheries, The Netherlands
Directorate General for International Cooperation, DGIS, The Netherlands

COOPERATING INSTITUTES

Indonesia:

AARD	Agency for Agricultural Research and Development
CSR	Centre for Soil Research
BARIF	Banjarbaru Research Institute for Foodcrops

The Netherlands:

LAWOO	Land and Water Group
ILRI	International Institute for Land Reclamation and Improvement
ICW	Institute for Land and Water Management Research
STIBOKA	Netherlands Soil Survey Institute
EUROCONSULT	Arnhem

Wageningen February 1989

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1. ANALYSES ON SOIL MATERIAL

1.1. DETERMINATION OF TOTAL ELEMENTAL CONTENT BY X-RAY FLUORESCENCE SPECTROMETRY

1.1.1. Principle

X-ray emission spectrometry is based on the fact that when a beam of X-rays is directed onto the surface of a specimen, secondary (or fluorescent) X-rays are emitted that contain wavelenghts characteristics of each element present in the sample. The radiation is collimated and directed to a detector in such way that the spectral lines may be measured individually. The most widely used method of detecting the wavelenghts and intensity of emitted X-rays is to use a crystal to diffract the X-rays according to Bragg's law and to scan through a range of angular positions using a gas-filled proportional counter or a scintillation counter as detector. This system is called the wavelenght-dispersive X-ray fluorescence spectrometry.

1.1.2. Apparatus

Use has been made of a Philips PW 1404/00 owned by the department of soil science and geology, Agricultural University Wageningen, the Netherlands.

1.1.3. Procedure

Only a few gram of soil sample is needed for the determination of total elemental content by X-ray fluorescence spectrometry. Before the actual analyses can start grinding has to be carried out and loss on ignition has to be measured. Herefore, the airdry or feezedried sample will be weighed and dried in an oven for 4.5 hours at a temperature between 450 and 900°C. At a temperature of 450°C loss on ignition is caused by the loss of rest water and the loss of organic matter. At a temperature of 900°C also strongly bonded (interlayer, crystalline) water will be lost, as well as easily destructable sulfur fractions. If strongly bonded water and/or easily destructable sulfur is expected to be present in significant amounts

drying at a temperature of 900°C is recommendable. After the loss on ignition is analysed a pearl is been made of the soil material at a temperature of approximately 1000°C.
With this pearl total elemental content is analysed with the Philips PW 1404/00.

1.1.4. Calculation

The results are normally expressed as weight percentages of the most common elemental oxide (f.i. Fe_2O_3, CaO). Weight percentages of each single element (f.i. Fe, Ca) can be obtained easily by recalculation using molecular weights of the different components.
Normally the macro-elements Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P and Ba are determined. Standard micro-elements which can be determined are V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Zr, Nb, Ba, La and Pb. Micro-elements are been expressed in ppm.

1.1.5. Accuracy

An analyses can be considered accurate if the cumulative elemental weight percentage falls in the range of 98 up to 102% of the total weight of the original soil sample used at the start of the experiment.

1.1.6. Literature

A.L. PAGE, R.H. MILLER and D.R. KEENEY (Eds.), (1982). Methods of soil analyses. Part 2 - Chemical and microbiological properties. Agronomy No. 9 (Part 2).

1.2. DETERMINATION OF MINERALOGICAL CONTENT BY X-RAY DIFFRACTION METHOD

1.2.1. Principle

The determination of the mineralogical content by rontgen diffraction analyses is, in contrast with the determination of the total elemental content by X-ray fluorescence analyses, a non-destructable method.

All soil minerals have their own characteristic wavelenghts series which can be measured. Normally the output of a rontgen diffraction analyses is presented on film (Guinier) or on plotpaper. Quantitative information about the amount of minerals can be gained if standard samples with known mineral amounts are analysed as well.

1.2.2. Apparatus

Guinier films have been obtained with the Philips PW 1120/00 in combination with a Nonius camera type Y860, owned by the department of soil science and geology, Agricultural University Wageningen.

1.2.3. Procedure

An airdry or freezedried soil sample of a few gram in weight can be used, after grinding it first. There is no need to analyse the loss on ignition.

1.2.4. Calculation

Measured wavelength series only have to be compared with tables in mineralogical handbooks or standard films to define which minerals are present in the soil sample.

1.2.5. Accuracy

If minerals are present in weight percentages below 0.5-1.0% determination becomes difficult so less accuracies will be obtained then.

1.2.6. Literature

A.L. PAGE, R.H. MILLER and D.R. KEENEY (Eds.), (1982). Methods of soil analyses. Part 2 - Chemical and microbiological properties. Agronomy No. 9 (Part 2).

1.3. DERMINATION OF SOIL MICROMORFOLOGY BY THIN SECTIONS

1.3.1. Principle

Soil micromorfology (types, distribution, amounts, sizes of primary and secondary minerals, coatings, humic fractions, micro- and macropores etc.) can be determined accurately by making thin sections.
A thin section is a very thin cross-section of the undisturbed soil obtained by grinding. Soil, being a soft and often friable material, needs to be artificially hardened to allow to be ground. A preparation of this kind must be of sufficient quality to allow accurate microscopic observations to be made at high magnifications. Further, detailed information on the soil micromorfology can be gained by using recently developed techniques such as electronmicroscopy (energy dispersive X-ray analyses, wavelength dispersive X-ray analyses) and use of the Quantimet 970.

1.3.2. Apparatus

Use will be made of thin sections, light-microscopy (Stiboka), electronmicroscopy (TFDL Wageningen and VU Amsterdam) and the Quantimet 970 (Stiboka).

1.3.3. Procedure

Undisturbed soil samples can be collected in the field with large soil columns, whereafter subsampling in the laboratory is possible with small metal boxes. Moisture in the soil samples can be removed with certain techniques, of which air drying, replacement with organic liquids, critical point drying, wet impregnation and freeze drying are examples. Impregnation and hardening is then the next step in the preparation of the thin sections. Processes such as sawing, grinding, mounting, polishing and covering are needed to make the hardened thin sections available for analyses.

1.3.4. Literature

A. JONGERIUS and G. HEINTZBERGER (1975). Methods in soil micromorfology. A technique for the preparation of large thin sections. Soil Survey Papers, No. 10

1.4. DETERMINATION OF ORGANIC CARBON CONTENT BY LOSS ON IGNITION

1.4.1. Principle

Freeze-dried, well mixed soil is put in a muffle furnace for about 4 hours at 550°C. At this temperature, carbonates, pyrite and most clay minerals are stable, so the loss in weight is attributable mainly to the oxidation of organic matter. There is also a possible loss in weight due to adsorbed and clay bonded water, for which a correction factor is available.

1.4.2. Apparatus

- porcelaine dishes with a lid (diameter about 50 mm, depth about 25 mm), provided with numbers;
- dry stove (temperature range 105°C; accuracy 5°C);
- muffle furnace (temperature range at least 550°C; accuracy 10°C);
- analytical balance (accuracy 0.1 mg);
- exsicator with silicagel;

1.4.3. Procedure

First glow the porcelain dishes at 550°C during 2 hours and cool them in an exsicator. Determine the empty weight of these dishes (m1). Weigh about 1.00 g of the sample material accurately into the previously glowed dishes and dry them at 105°C during the night. Cool the dishes in a dry stove during minimal 45 minutes and weigh the dish plus the dried soil (m2). Place the dishes in the muffle furnace and raise the temperature gradually till 550°C. Glow during 3 hours at this temperature. First cool the porcelain dishes by air, followed by a minimun stay of 45 min in an exsicator whereafter the weight of the dishes plus glowed soil (m3) can be determined.

1.4.4. Calculation

Calculate the loss of weight by glowing (GL) with the next formula:

$$GL = \frac{m2 - m3}{m2 - m1} \cdot 100\%$$

in which: GL = loss of weight by glowing at 550°C in % ($m.m^{-1}$) of the stove-dried soil
m1 = weight of empty previously glowed dish (g)
m2 = weight of dish and the stove dried soil (g)
m3 = weight of dish and the glowed soil (g)

The calculation of the organic carbon content needs a correction factor for the loss of water out of the anorganic fraction of the soil:

$$OC = GL - (0.3 + 0.063 \cdot LF)$$

in which: OC = organic carbon content in % ($m.m^{-1}$)
GL = loss of mass by glowing at 550°C in % ($m.m^{-1}$)
LF = clay fraction of the soil in % ($m.m^{-1}$)

1.4.5. Accuracy

Maximum allowed difference in duplo determinations:

% loss by glowing	allowed difference
0.00 - 15.00	0.75 %
> 15.00	5.00 %

1.4.6. Literature

NEN 5754 (1988), Soil: determination of organic matter as loss-on-ignition.
STIBOKA (1982), Humus content by glowing at 500 oC. Department of soil chemistry and clay mineralogy.

1.5. DETERMINATION OF TOTAL PYRITE (FES_2) CONTENT BY STIBOKA METHOD

1.5.1. Principle

First, all Fe containing minerals, except for pyrite, are soluted by adding a mixture of concentrated HF and HCl 1:1. Then pyrite content is determined in the residue by measuring the Fe content after destruction at 800∘C.

1.5.2. Reagents en apparatus

- distilled water;
- a mixture of acids: mix 40 ml HF conc. (40%) with 40 ml HCl conc. (37%) in a polyethylene flask;
- a saturated boric acid solution: add about 30 grams of H_3BO_3 to 500 ml water. Shake for about 2 hours and control if the solution is saturated;
- muffle furnace (temperature range 1000 oC; accuracy 10∘C);
- analytical balance; accuracy 0.1 mg;
- porcelain disks of about 25 ml;
- oven;
- electrical boiling plate;
- glassware;

1.5.3. Procedure

Pulverize carefully 2 grams of the soil sample in a mortar and weigh 50 - 200 mg accurately in a 10 ml polyethylene cup with lid. Read the safety instructions in the handbook. Add 2 ml of the acid mixture and close the cup. Homogenize by swirling around and place the cup for 2 hours in the stove at 50∘C. Transfer the content to a quantitative filter (589-3 Blue

Ribbon) in a hood provided with a gas-wash installation. Add directly 20 ml saturated boric acid solution. Wash the filter at least 4 times with soured (HCl) water till there are no yellow spots anymore.
Ash the filter at 800°C in a porcelain disk during 1 hour and solute the residue in 10 ml concentrated HCl. Evaporate till the volume is reduced to 1 a 2 ml on a electrical boiling plate. Dilute with water to about 15 ml. Transfer this solution in a measuring flask of 100 ml, fill to the line and homogenize. Measure the iron content in the solution with use of the AAS or ICP.

1.5.4. Calculation

% pyrite = (A - 0.03) . (100/M) . 2.1486

in which: A = the quantity Fe in 100 ml of the measuring solution (mg)
M = sample weight (mg)

N.B. The correction factor of A with 0.03 mg iron is an approximation of that part of iron that remains in the filter. This factor is in principle dependent of the filter and of the wash-procedure. It deserves recommendation to drain the filter every time after a wash with acidified water.

1.5.5. Accuracy

Standards and duplo's may differ not more than 10 %.

1.5.6. Literature

STIBOKA (1982), Pyrite (FeS_2) determination. Department of soil chemistry and clay mineralogy.

1.6. DETERMINATION OF TOTAL SULPHUR CONTENT BY PARTIAL FUSION OF ALL SULPHUR TO SULPHATE

1.6.1. Principle

Conversion of all sulphur compounds to sulphate by partial fusion in a mixture of sodium carbonate and potassium nitrate at 700°C.

1.6.2. Reagents and apparatus

- mixed reagent; solid Na_2CO_3 and KNO_3 in 10 : 1 ratio, mix thoroughly 100 g of Na_2CO_3 and 10 g KNO_3;
- HCl; c(HCl) = 2.0 $mol.l^{-1}$ (2.0 N) dilute 40 ml of concentrated HCl (38%) with water to a volume of 250 ml;
- a muffle furnace; temp. range at least 700°C;
- centrifuge; range at least 3000 rpm;
- porcelain disks;
- polypropylene centrifuge tubes;
- boiling water bath;
- HPLC, suitable to measure sulphate;
- glassware;

1.6.3. Procedure

Weigh separately about 200 mg freeze dried fine earth (< 2 mm) and 1.0 g of mixed reagent. Transfer 4/5 th of the mixed reagent with the weighed sample material into an 18 ml high model porcelain cup and mix thoroughly. Cover the surface of the mixture with the remaining 1/5 th of the mixed reagent. Place the cup in a muffle furnace, heat to 700°C and maintain at that temperature for exactly 40 minutes. Remove the disk and cool. Transfer the material into a 50 ml polypropylene centrifuge tube using a part of a 10 ml portion of 2 N HCl. Place the tubes in a boiling water bath until CO_2 effervescence has ceased. Centrifuge at 3000 rpm for 30 minutes. Decant the clear supernatant into a 100 ml volumetric flask. Wash the residue by means of 25 ml water, centrifuge and decant the washing solution into the volumetric flask. Dilute with water to the mark and homogenize. Pipet 10.0 ml of the extract in a 50.0 ml volumetric flask dilute with water to the mark and homogenize. Measure sulphate by means of the HPLC or if this causes difficulties use the photometric determination of sulphate content.

N.B. Potassium nitrate is an efficient oxidizing reagent and lowers the melting point of the sodium carbonate so that partial fusion occurs without excessive decomposition of silicates from the soil of the porcelain cup. The Na_2CO3/KNO_3 ratio and the temperature are critical. If an excess of potassium nitrate is used, or, if the temperature is allowed to rise above 700°C, a hard melt is formed and the extraction of sulphate is made more difficult. Moreover, large amounts of silicate are mobilized and may interfere the assay of sulphate.

1.6.4. Calculation

Percentage of sulphur in mass of the sample is calculated with the next formula:

$$S = 0.167 \,.\, A/B \,.\, 100\%$$

in which S = sulphur content (weight %)
A = concentration of sulphate in solution ($mg.l^{-1}$)
B = quantity of sample (mg)

1.6.5. Accuracy

An accuracy of less than 5 percent is reasonable.

1.6.6. Literature

BEGHEIJN L.Th. (1980). Methods of chemical analyses for soils and waters Department of soil science and geology, Agricultural University, Wageningen, the Netherlands

GRANT C.J. and H.L. YEUNG (1971), Agricultural Science. pp. 256-264.

1.7. DETERMINATION OF TOTAL CARBONATE CONTENT BY CO_2 PRODUCTION

1.7.1. Principle

By adding an excess amount of hydrochloric acid to a soil sample CO_2 is produced by the decomposition of carbonates. The produced CO_2 is measured volumetrical by the method of Scheibler. Carbonates which can be present in the soil are for instance calcite and aragonite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$). The total carbonate content is usually expressed as fraction $CaCO_3$. If more information is needed which carbonate minerals are actually present in the soil X-ray analyses is a good complementary alternative to carry out.

1.7.2. Reagents and apparatus

- hydrochloric acid solution: mix 1 part HCL (38%) with 3 parts of water
- $CaCO_3$ quality GR
- Scheibler apparatus (see fig. 1)

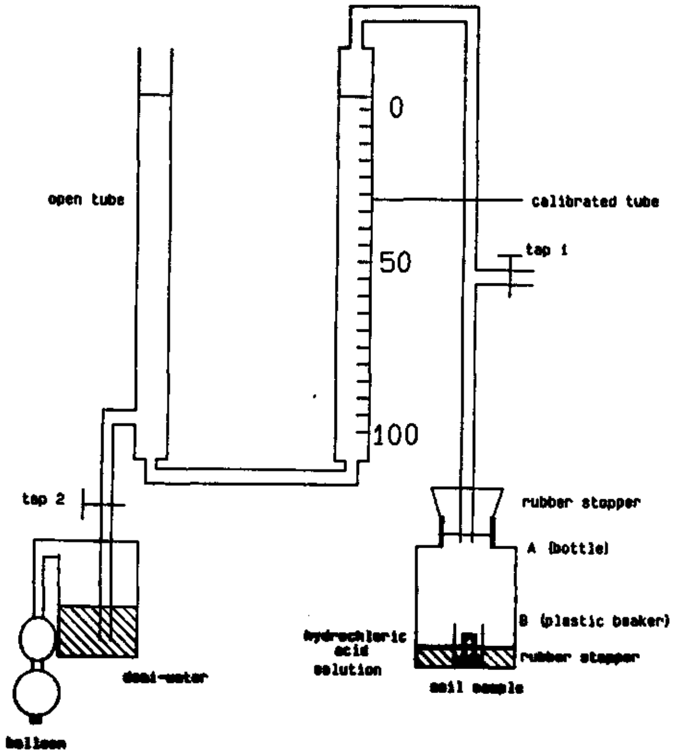

Fig. 1. Scheibler apparatus for measuring CO_2 production

1.7.3. Procedure

Weigh about 1 gram of soil sample in a plastic beaker (B) (see Figure 1) of 10 ml. Fill the bottle (A) of 200 ml with 30 ml hydrochloric acid solution. Make the beaker heavier with a rubber stop. Bring the beaker by use of a pair of tongs in the bottle. Open tap 1 and bring the liquid level up to height "0" by use of the balloon. Close now tap 1 and open tap 2. Wait till the level has adjusted itselfs again. Turn over the beaker and shake the bottle so that the sample is well mixed up with the hydrochloric acid solution. Repeat this several times during 5 minutes. Bring the level in the open tube up to about the same height as in the calibrated tube. Wait for about 15 minutes and swirl the bottle several times till there is no change in level anymore. Bring the level in the open tube up to exactly the same height as in the calibrated tube. Read the level in this tube (accuracy 0.1 ml).
Measure at the same time a standard sample ($CaCO_3$) of 100 and 200 mg.

1.7.4. Calculation

Calculate with the standard samples the quantity of ml's CO_2 (x) produced by one gram carbonate (i.e. calcite as reference for all carbonates). Keep in mind that this amount is temperature and pressure dependent. The produced quantity CO_2 by the soil sample is called "y" ml. The carbonate fraction ($CaCO_3$) is then:

$CaCO_3$ perc. = y/x . 100%

1.7.5. Accuracy

An accuracy of a few percentages of the measured value is reasonable.

1.7.6. Literature

STIBOKA (1970). Determination of carbonate content in soil samples.
Department of soil chemistry and clay mineralogy

1.8. DETERMINATION OF THE CEC AND BASE SATURATION BY UNBUFFERED $BACL_2$ METHOD

1.8.1. Principle

The determination of the CEC as described in this procedure is a modification of the method proposed by GILLMAN (1979). This method describes a procedure for the determination of the CEC of soil samples at the pH of the soil at low ionic strenghts (about 0.01 M).
The soil is first saturated with Ba by adding an excess amount of $BaCl_2$-solution of 0.1 M to it and shake it well for one hour. This procedure has to be repeated at least three times. Thereafter the soil is equilibrated with a final BaCl-solution of about 0.01 M. Subsequently a known excess of 0.02 M $MgSO_4$ is added. All the Ba present, in the solution as well as adsorbed, is precipitated as the highly insoluble $BaSO_4$ and the adsorption sites are now completely occupied by Mg. The excess of Mg is measured by AES/ICP. In the 0.1 M $BaCl_2$ extract of the soil Na, K, Ca, Mg, Mn, Fe and Al can be measured.

1.8.2. Reagents and apparatus

- bariumchloride solution, 0.1 M. Dissolve 24.43 g of $BaCl_2.2H_2O$ in water and fill to 1000 ml with water;
- bariumchloride solution, 0.0025 M. Dilute 25 ml of the 0.1 M bariumchloride solution to 1000 ml;
- magnesium sulphate solution, 0.02 M. Dissolve 4.9296 g $MgSO_4.7H_2O$ in water and dilute to 1000 ml.

1.8.3. Procedure

Transfer 2.50 g of freeze-dried soil (particle size < 2 mm) to a polythene centrifuge tube of about 50 ml. Note the weight of bottle and soil (W1 g). Add to the soil 30 ml of the 0.1 M bariumchloride solution. Stopper the tube tightly and shake for 1 h. Balance the tubes and centrifuge at 2300 rpm for 10 min. Transfer the supernatant liquid to a 100 ml volumetric flask. Add again to the soil 30 ml of the 0.1 M bariumchloride solution and repeat the shaking and centrifugation. Transfer the supernatant liquid to the same 100 ml volumetric flask. Repeat this addition of 30 ml, shaking and centrifugation a third time and add the supernatant liquid again to the same 100 ml volumetric flask. Fill the flask with 0.1 M bariumchloride solution. Mix and store it for the determination of the occupation grade of the complex. Prepare also a blank.

Measure in this solution (A) the concentrations of Al, Ca, Mg, Fe, Mn, Na and K. Al, Ca, Mg, Fe, Mn, Na are measured with ICP/AES. K with AAS. Add to the soil 30 ml of the 0.0025 M bariumchloride solution and shake overnight. (The barium concentration in the equilibrium solution will be about 0.01 M if 2.5 ml solution is left in the soil sample). Balance the tubes and centrifuge at about 2300 rpm for 10 min. Decant the supernatant.

Weigh the tubes with content (soil) (W2 g). Add to the soil 30 ml of the 0.0200 M magnesiumsulphate solution and shake for 2 h. Balance the tubes and centrifuge at 2300 rpm for 10 min. Decant the supernatant solution in a polythene bottle.

Pipette 10 ml of this solution and the blanks into 100 ml volumetric flasks. Fill to the mark with destilled water and homogenize. Measure in the diluted samples (B) and the blanks the magnesium concentration by ICP/AES.

1.8.4. Calculation

The exchangeable bases content in the soil samples in meq+.kg^{-1} is calculated according to:

Na(exch) = 4.35 . (a-b)/w
K(exch) = 2.56 . (a-b)/w
Mg(exch) = 8.23 . (a-b)/w
Ca(exch) = 4.99 . (a-b)/w
Mn(exch) = 3.64 . (a-b)/w
Fe(exch) = 3.58 . (a-b)/w
Al(exch) = 11.12 . (a-b)/w

in which: Y(exch) = exchangeble "Y" of the soil (meq.kg^{-1})
a = concentration of "Y" in the extracts (mg.l^{-1})
b = concentration of "Y" in the blank (mg.l^{-1})
w = weight of soil material (g)

Remarks: The valence of iron at the complex under anaerobic conditions is 2.

The concentration of magnesium in the sample solutions should be corrected for the effect of the volume of the liquid retained by the centrifuged soil after having been treated with 0.0025 M $BaCl_2$.

Corrected concentration A2 = A1 . (30 + W2 - W1)/30 $(mmol.l^{-1})$

In which: A1 = concentration of Mg $(mmol.l^{-1})$

The CEC of the soil is:

CEC $(meq+\ kg^{-1})$ = (B-A2) . 600/w

In which: A2 = concentration of Mg in the sample $(mmol.l^{-1})$
B = concentration of Mg in the blank $(mmol.l^{-1})$
w = weight of soil sample (g)

Remarks:
- If the CEC exceeds 400 $meq.kg^{-1}$, the determination should be repeated using less soil.
- $MgSO_4.7H_2O$ may loose crystal water on standing. The reagent should be standarized.

1.8.5. Accuracy

Standards and duplo's may differ not more than 5 per cent.

1.8.6. Literature

GILLMAN, G.P. (1979). A proposed method for the measurement of exchange properties of highly weathered soils. Austr. J. Soil Res. 17:129-139.

HOUBA, V.J.G., J.J. VAN DER ZEE, I. NOVOZAMSKY, I. WALINGA (1988). Soil and plant analysis. Part 5; soil analysis procedures. Department of soil science and plant nutrition, Wageningen Agricultural University, The Netherlands pp. 6-25/6-31.

2. ANALYSES ON SOIL MOISTURE

2.1. DETERMINATION OF K CONTENT BY ATOMIC ABSORPTION SPECTROMETRY (AAS)

2.1.1. Principle

Atomic absorption is determinated by measuring at 766.5 nm after atomizing in an air acetylene flame.
Correction of the signal for non-atomic absorption is not necessary. The potassium content is defined as the fraction which is in solution.
Ionisation of potassium in the flame is surpressed by adding cesium.

2.1.2. Reagents and apparatus

- potassium solution, K content 1000 $mg.l^{-1}$; dilute a potassium standard solution in 1 liter distilled water and homogenize;
- make a standard potassium solution with the following concentrations 0.5, 1.0, 1.5, 2.0 and 2.5 $mg.l^{-1}$;
- an atomic absorption spectrometer, suitable to measure at 766.5 nm, provided with a burner for an air acetyleneflame;
- a hollow cathode lamp for potassium.

2.1.3. Procedure

Adjust the atomic absorption spectrometer at the right wavelenght to measure potassium.
Nebulize the blank, the standards and the samples in an oxidizing air acetylene flame and determine the atomic absorption by 766.5 nm. Make a calibration graph whereby the absorption values are corrected for the absorption of the blank. Correct the measured absorption value of the samples for the blank and read the potassium content out of the calibration graph.

2.1.4. Calculation

Calculate the potassium content according to:

$$C = C' . f$$

in which: C = potassium content of the sample
C' = potassium content in the diluted sample
f = diluting factor

2.1.5. Accuracy

The accuracy of the measurements depends on the apparatus, as can be read in the operation manual.

2.1.6. Literature

NEN 6424 (1988). Water determination of potassium content by atomic absorption spectrometry (flame technique).
VARIAN TECHTRON PTY. LTD (1979). Analytical methods for flame spectroscopy. Publication No. 85-100009-00
VARIAN TECHTRON PTY. LTD (1987). SpectrAA-300/400 Operation Manual. Publication No. 85-100697-00

2.2. DETERMINATION OF Na, Ca, Mg, Fe, Mn AND Al CONTENT BY AES/ICP TECHNIQUE

2.2.1. Principle

Atomic emission is measured at the right wavelenght for each element after atomizing in an argonplasma (inductively coupled plasma). An advantage of this technique is the possibility to measure more elements in one sample.

2.2.2. Reagents and apparatus

- a standard solution based on Titrisol standards with concentrations of 100 ppm Na, 100 ppm Ca, 10 ppm Mg, 10 ppm Fe, 10 ppm Mn and 10 ppm Al;
- an ICP emission spectrometer.

2.2.3. Procedure

For use of the ICP emission spectrometer see the methods manual, and ICW Note 1784. The next wavelenghts have been used because at this values minimum interferences occur.

Element	Wavelength
Na	589.59
Ca	315.89
Al	309.27
Mn	293.93
Mg	285.21
Fe	239.56

2.2.4. Calculation

The ICP emission spectrometer calculates the various contents in the samples. The results of the measurements are given as concentrations in ppm.

2.2.5. Accuracy

A difference in duplo samples less than 2 percent is allowed.

2.2.6. Literature

HAMMINGA, W. (1987). Users manual for the inductively coupled plasma/atomic emission spectrometer (ICP/AES). ICW Note 1784.

ALLIED ANALYTICAL SYSTEMS (1984). Inductively coupled plasma, methods manual.

2.3. DETERMINATION OF CL, NO_3 AND SO_4 CONTENT BY HIGH PRESSURE LIQUID CHROMOTOGRAPHY

2.3.1. Principle

Selective seperation of anions over a reversed phase column with a 1 mM phtalic acid and 1 mM tetrabutylammoniumjodide eluting solution. The peaks are detected by a UV-cell.

2.3.2. Reagents and apparatus

- Stock standard solution: 500 ppm of Cl^-, NO_3^- and SO_4^{2-}:
  - a. dry sodiumchloride, NaCl, during 1 h at 150°C. Cool in an exsicator and weigh 0.8242 g;
  - b. dry sodiumnitrate, $NaNO_3$, during 1 h at 120°C. Cool in an exsicator and weigh 0.6854 g;
  - c. dry potassiumsulphate, K_2SO_4, at 400°C for 2 hours. Cool in an exsicator and weigh 0.9071 g.

  Transfer the salts to a volumetric flask of 1 liter, fill with distilled water to the mark and mix thoroughly. If stored in a cool and dark place the solution is tenable for at least 2 months.
- Standard solution: 50 ppm of Cl^-, NO_3^- and SO_4^{2-}.
  Dilute 10 ml of the stock solution in a 100 ml volumetric flask.
  Fill to the mark and homogenize.
  This solution is tenable for at least 2 weeks if stored in a cool and dark place.
- Eluting solution: 1 mM phtalic acid, 1 mM tetrabutylammoniumjodide (tbaI).
  Weigh 1.329 g of phtalic acid and 2.955 g of tbaI and solute this in 8 liter of distilled water. Adjust the pH of the solution at exactly 6.0 by adding very carefully 0.1 N NaOH.
  Store the solution in a cool and dark place. Also when using the eluting solution see to it that it is held away from light.
- Acetonitrile for HPLC.
- HPLC pump, which can maintain a constant eluting flow at a pressure of 1 to 5 MPa. The flow must have a range from 0.00 to 2.00 $ml.min^{-1}$.
  Spectroflow 400.

- UV detector; Spectroflow 773.
- Injection tap; Rheodyne 7125.
- Reversed phase column: Chromsep HPLC column;
  packing material: ChromSpher C18;
  typical partical size: 5 µm;
  lenght: 100 mm;
  internal diameter: 3 mm;
  external diameter: 8 mm;
  column material: glass;
  maximum pressure: 20 MPa.
- System to control the apparatus and to process the data by integrating the peaks. Model 2600 Chromatography Software, Nelson Analytical Inc..

2.3.3. Procedure

The samples must be prepared in little sample bottles of 2 ml by injection after fittering over 0.045 µm fitter.
The HPLC system is first washed for 24 hours with acetonitrile (toxic). Hereafter, rinse the system for exactly 3 minutes with water, followed by again 24 hours with the eluting solution. The UV lamp needs a warm-up period of about 2 hours. After this time you can start up the calibration of the apparatus and measure the samples by following the provided instrumental directions.
When finished, again rinse the system for a few minutes with water followed by at least 24 hours with acetonitrile.

2.3.4. Calculation

$$\text{mg anion} = \frac{\text{peak area of anion in sample solution}}{\text{peak area of anion in calibration sol.}} \cdot \text{mg anion in cal. sol.}$$

2.3.5. Accuracy

The accuracy depends on the used apparatus, however, an accuracy of 5% must be possible with modern HPLC apparatus.

2.3.6. Literature

NEN 6588 (1988). Rain water - Determination of chloride, phosphate, nitrate and sulphate content by ion chromatography

BEGHEIJN, L.Th. (1980). Methods of chemical analyses for soils and waters. Agricultural University Wageningen, department of soil science and geology, the Netherlands

USERS MANUAL HPLC.

2.4. DETERMINATION OF SO_4 CONTENT BY PHOTOMETRICAL METHOD

2.4.1. Principle

Sulphate precipitates in a hydrochloric acid medium with barium chloride to form bariumsulphate. This is kept in suspension with a conditioning reagent. The absorbance of light by the suspension is measured with a spectrophotometer at 420 nm. The sulphate concentration is quantified by comparison of the reading with those of standard solutions (standard curve).

2.4.2. Reagents and apparatus

- Spectrophotometer suitable to measure at a wavelenght of 420 nm. Cell length 1 cm.
- Magnetic stirrer.
- Stopwatch.
- Conical flasks of 100 ml.
- Conditioning reagent: Dissolve 75 grams NaCl in 800 ml distilled water. Add 30 ml concentrated hydrochloric acid, 100 ml ethanol and 50 ml glycerine (glycerol) and mix thoroughly.
- Bariumchloride ($BaCl_2$) crystals.
- Standard sulphate solution 1000 ppm. Weigh 1.479 g Na_2SO_4 and dissolve in 1 liter distilled water (measuring flask). The Na_2SO_4 must be dried at 300°C for at least 4 hours. Pipette from this solution 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 ml in measuring flasks of 100 ml.
  This gives solutions of 10 up till 100 ppm sulphate.

2.4.3. Procedure

The following procedure should be used for the standard solutions as well as for the samples.

- pipette 20 ml of the sample in a conical flask of 100 ml;
- add 2 ml of conditioning reagent;
- add a magnetic rod and place the flask on a stirrer. Place a funnel on the flask;
- add 0.10 g bariumchloride;
- stir exactly for 1 minute. Adjust during this period the spectrophotometer on 0.000 using the blank. Use 20 ml of the sample as a blank and add all the reagents except for the barium chloride.
- measure the absorbance on the spectrophotometer at 420 nm. Read during 4 minutes. Take the maximum reading obtained during this period. If the absorbance is still getting higher measure the absorbance after 4 minutes (this is approxiamately 5 minutes after adding the barium chloride). If the reading is higher then the reading of the highest standard, dilute the sample.

2.4.4. Calculation

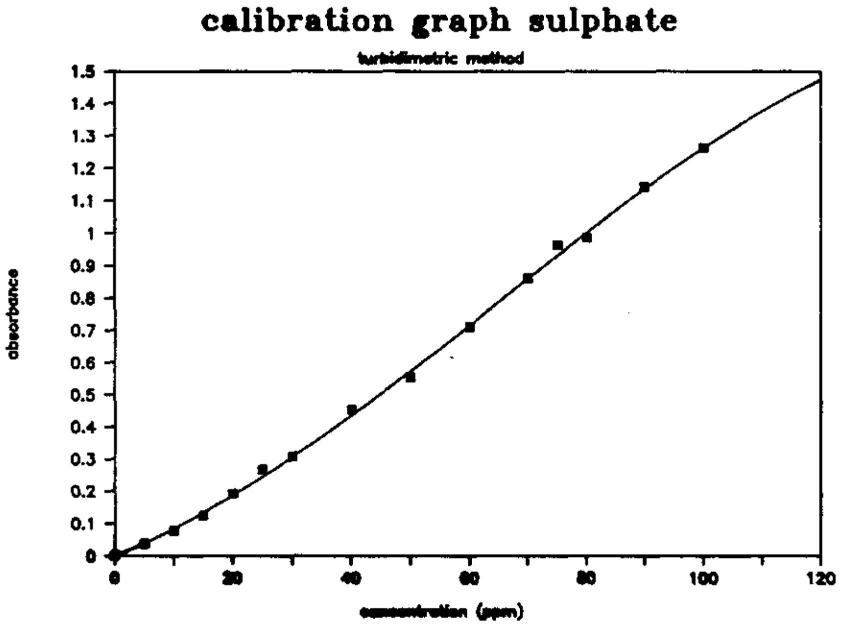

Fig. 1. Calibration curve for SO_4 analyses

Make a calibration graph as shown in Figure 2.
Read the amount of sulphate from the curve. Multiply it with the diluting factor which is used.

2.4.5. Accuracy

Results are reproducible within 5 per cent of the sulphate concentration when interferences are absent. The results are normally within an accuracy of about 10 % of the sulphate concentrations measured under the best analytical conditions in solutions with SO_4 concentrations not exceeding 10 $mg.l^{-1}$. Accuracy decreases rapidly for concentrations above 40 $mg.l^{-1}$.

2.4.6. Literature

TOORN A. VAN DE, K. NUGROHO and J. HARMSEN (1988). Methods for the determination of chemical composition of water samples from column experiments. ICW Note 1863.

AMERICAN PUBLIC HEALTH ASSOCIATION INC. (1960). Standard methods for the examination of water and wastewater, 11th ed.

2.5. MEASURING OF pH

2.5.1. Principle

Hydrogen ions cause a potential difference at a glass-electrode/ reference-electrodesystem, which can be recalculated to pH values.
The difference in potential is measured with an electronic voltmeter, provided with a pH-scale.

2.5.2. Reagents and apparatus

- a pH meter with steepness correction and temperature compensation, for instance the pH 535 multical;
- a glasselectrode and a reference electrode, or combined;
- a thermosensor;

- at least 2 of the next buffersolutions:
  - . Buffer-Titrisol for 500 ml/Buffer solution pH 4.00 (citrate-hydrochloric acid) Accuracy 0.02 pH;
  - . Buffer-Titrisol for 500 ml/Buffer solution pH 7.00 (phosphate) Accuracy 0.02 pH;
  - . Buffer-Titrisol for 500 ml/Buffer solution pH 9.00 (boric acid/potassiumchloride-sodiumhydroxide) Accuracy 0.02 pH store the buffersolutions in a polyethylene bottles in a refrigerator.

2.5.3. Procedure

Measure the pH as soon as possible after collecting a sample.
Calibrate the pH meter, as mentioned in the manual of the pH meter. Use by preference the mentioned buffer solutions. Carry out the calibration at room temperature or at the temperature at which will be measured. Measure the pH, as mentioned in the users manual. Measure at room temperature. If you measure at a different temperature mention this in the report.

2.5.4. Accuracy

Measuring range: pH 0.00 - 14.00.
Accuracy apparatus: 0.01 pH.

2.5.5. Literature

NPR 6616 (1982), Water and sludge - Routine determination of pH Users manual for a microprocessor pH-meter, pH535 Multical.

2.6. DETERMINATION OF ELECTRIC CONDUCTIVITY (EC)

2.6.1. Principle

The electric conductivity is related to the total concentration of the ionized substances in a water sample and is dependent on the temperature at which the measurement is made. Electric conductivity is defined as the reciprocal of the resistance measured between two electrodes 1 cm apart and 1 sq cm in cross section.

2.6.2. Reagents and apparatus

- automatic electric conductivity meter (PW 9506 Philips);
- distilled or deionized water with a electric conductivity not exceeding 1 mS.m^{-1};
- standard measuring cell with integrated thermosensor, K = 1.0 cm, suitable for the total slope till 2.10^3 mS.cm^{-1}.

2.6.3. Procedure

Each conductivity measuring cell has a characteristic cell constant K (cm) which depends on the geometry of the electrode surfaces. The cell constant cannot be adjusted. In this case the constant control is adjusted to 1.00. See the users manual. Measure with automatic temperature compensation. The value given by the apparatus is the conductivity at reference temperature (20°C).

2.6.4. Accuracy

The precision and accuracy with which the conductivity of water can be determined depends upon the equipment used. An accuracy of about 2% is possible with the available instrument.

2.6.5. Literature

NEN 6412 (1979), Drinking water determination of conductivity.
Users manual of the Philips PW 9506 digital conductivity meter.

2.7. ELECTROCHEMICAL DETERMINATION OF DISSOLVED OXYGEN CONTENT

2.7.1. Principle

An oxygen electrode, consisting of 2 metal electrodes in an electrolyte filled cell, fenced off by a semi-permeable membrane, is placed in the water. The membrane is permeable for oxygen and a few other gasses but almost impermeable for water and solutes.
As a consequense of the difference in potential, generated by the electrodes itselfs (galvanic cell), or by an external voltage source (polarografic cell), electrons are moving towards the kathode, where oxygen is being reduced, according to

$$O2 + 2\ H2O + 4\ e \rightarrow 4\ OH^-$$

The diffusion current (which only occurs when at the same time at the anode an oxidation reaction takes place), is an function of the partial pressure of the molecular oxygen in the sample at a given temperature.

2.7.2. Reagents and apparatus

- An electrolyte solution.
- An oxygen-meter (WTW Microprocessor Oximeter OXI96), consisting of:
  - . an electrode based on the principles of the polarografic cell (p.e. Ag-Au), provided with an automatic temperature correction, allowed sample temperature: 0 - 50°C temperature compensation: automaticly between 0 - 50°C detection limit: 0.02 mg.l^{-1};
  - . a meter, which gives the concentration of the soluted oxygen or the saturation percentage:
    range O_2: 0 - 199 % saturation
    0 - 50.0 mg.l^{-1}
    range temp.: - 5.0 - 45.0°C
  - . magnetic stirrer

2.7.3. Procedure

Place the electrode in a water sample and wait till the reading is stable. Follow the instructions in the users manual.
Using the electrode, consider the next points:

- take care that the convection current around the membrane is stable and fast enough during the measurements and the calibration;
- prevent, when changing the membrane, contamination of the electrode parts and enclosing airbubbles under the membrane, which can cause a lowered response and a high rest current;
- prevent touching the membrane with your fingers.

Calibration: follow the instructions of the manual.
Because the electrode has no zero-current, a one point calibration is sufficient. Place the electrode in the Oxical calibration cell and wait a few minutes. Set the oxygen-meter with the right knob at the front to 102 %.
The instrument is now ready for measurements.

2.7.4. Accuracy

Accuracy O_2 : < 1 % or < 0.1 $mg.l^{-1}$
Accuracy temp.: 0.2°C

2.7.5. Literature

Users manual WTW Digital oxygen meter OXI91.
NEN 6632 (1986). Water determination of oxygen content and oxygen saturation percentage, electrochemical method.
American Public Health Association Inc. (1960). Standard methods for the examination of water and wastwater.

2.8. DETERMINATION OF ORGANIC AND INORGANIC CARBON CONTENT BY TOC ANALYZER

2.8.1. Principle

Anorganic carbon
Conversion of bicarbonates and carbonates into carbondioxide by phosphoric acid and measuring of the produced CO_2 by IR-spectrometry comparing

recorded peak heights of samples with those of standards. Results can be expressed either as total dissolved inorganic carbon ($[CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$) or each of the fractions estimated from pH, temperature and ionic strenght.

The oxidation is summarized as follows:

$$HCO_3^-,\ CO_3^{2-} \xrightarrow[\text{fast}]{H^+} CO_2,\ H_2O$$

$$CO_2,\ H_2O \xrightarrow[\text{slow}]{\text{sparge}} CO_2\ (\text{gas}) + H_2O$$

The total amount of carbondioxide produced is measured.

Organic carbon

Conversion of organic carbon into carbondioxide by using a UV promoted persulphate oxidation. The carbondioxide produced is measured by infrared detection. Results are given in ppm C.

The low temperature UV promoted persulphate oxidation of organics can be summarized as follows:

1. Formation of main oxidants:
   a. $S_2O_8^{2-} + hv \text{ ----> } 2\ SO_4^-.$
      SO_4^- is a very stable and strong oxidizing agent;
   b. $H_2O + hv \text{ ----> } H. + .OH$
      $SO_4^-. + H_2O \text{ ----> } SO_4^{2-} + .OH + H^+$ in which hv = energy of the UV lamp.
2. Excitation of organics:
   $R + hv \text{ ----> } R^*$
3. Oxidation of organics:
   $R^* + SO_4^-. + H_2O \text{ ----> } n\ CO_2 + \ldots\ldots$ The total amount of produced carbondioxide is measured.

2.8.2. Reagents and apparatus

- total organic analyzer Dohrmann DC-180;
- printer HP ThinkYet;
- infrared gas analyzer ACS model 3300 dual range;
- carrier gas supply; air;
- gas filter filled with Soda lime pellets with indicator. The filter takes out the carbondioxide in the air;
- soda lime pellets GR;
- reagent water: organic free deionized or distilled water;
- potassium persulphate reagent, 2%: Prepare by dissolving 20 grams of reagent grade potassium persulphate ($K_2S_2O_8$) in 1 liter of reagent water. Add 2 ml of concentrated phosphoric acid and mix well. These quantities need not be measured with great accuracy; about 5% is sufficiently close. The desired pH is about 3;
- organic carbon standards: prepare a 1000 ppm C stock standard by weighing 2125 mg of dried potassium hydrogen phthalate ($C_8H_5O_4K$). Transfer the KHP to a 1000 ml volumetric flask and dissolve with 50-75 ml water. Add 0.1 ml conc. phosphoric acid and fill to the mark. Make a 100 ppm C standard by diluting 10 ml stock solution in a 100 ml volumetric flask with reagent water;
- inorganic carbon standards: dissolve 4404 mg of anhydrous sodium carbonate, Na2CO3, in a 1.0 liter volumetric flask in about 500 ml water. Add 3497 mg of sodium hydrogen carbonate, NaHCO3, and dilute to the mark. This is the stock solution. Dilute this stock solution 10 times to get the standard solution of 100 ppm C.
- 20% phosphoric acid; dilute 20 ml 85% phosphoric acid to 100 ml with water.

All stock solutions are tenable for a month if stored in a cool and dark place. The standards need to be refreshed every week.

2.8.3. Procedure

The samples have to be prepared in the tubes of the TOC meter and immediately closed by a cap or parafilm, cq laboratory film, and stored in a cool and dark place. The analyses are carried out according to the prescriptions of the manufacturer of the apparatus. After calibration of the apparatus check the analyses by measuring a standard after each ten samples.

2.8.4. Accuracy

Range : 10 ppb to 30.000 ppm.
Accuracy: 2 % of measured value or 5 ppb, depending on the value of the measurement.

2.8.5. Literature

NPR 6522 (1986), Water determination of organic and inorganic carbon content with TOC-apparatus and measurement of the performance characteristics of those apparatus.
DOHRMANN (1987). DC-180 TOC Analyzer Systems Manual

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RESEARCH ON ACID SULPHATE SOILS IN THE HUMID TROPICS

SCIENTIFIC REPORTS

1 Bronswijk J.J.B. & C.J.Ritsema 1987
Modeling physical and chemical processes in acid sulphate soils, Analysis of important parameters and first outline of simulation model.

2 Ritsema C.J., J.J.B.Bronswijk & K.Nugroho 1988
Proposal for column experiments to study physical and chemical processes in acid sulphate soils.

3 Toorn A. van den, K.Nugroho & J.Harmsen 1988
Methods for determination of chemical composition of water samples from column experiments. Also available in Indonesian.

4 Bronswijk J.J.B., C.J.M.Konsten, K.Nugroho & C.J.Ritsema 1988
Set up of field experiments in South Kalimantan

5 Bouter P. 1988
Colorimetric determination of aluminium content at high iron concentrations.

6 Bakker D.M., P.Bouter, J.J.B.Bronswijk, Ida Bagus Aribawa, C.J.M. Konsten, K.Nugroho, Supardi Suping & C.J.Ritsema 1988
Interim results column experiments Wageningen-Banjarbaru.

7 Sevenhuysen R.J. & R.A.L.Kselik 1988
Inventory of boundary conditions for water-management activities in the Pulau Petak island, Kalimantan.

8 Bouter P. & C.J.Ritsema 1989
Chemical analyses on soil material and soil moisture.

MISSION REPORTS

1 Wijk A.L.M. van, C.J.Ritsema & J.J.B.Bronswijk 1987
Report on an introductory mission to the counterpart institutes CSR-Bogor and BARIF-Banjarbaru and the tidal swamp area of Pulau Petak, South Kalimantan, Indonesia.

2 Bos M.G. 1987
Report on the first coordination mission.

3 Sevenhuysen R.J. & R.Kselik 1988
Report on the initiation mission of Phase I, water management component.

4 Andriesse W. 1988
First mission report, survey component.

5 Eelaart, A.L.J. van den, 1988
Selection of sites for detailed research and identification of major research subjects in the Pulau Petak area, Southern Kalimantan.

6 Pons, L.J. 1988
Soil and landscape genesis in the Pulau Petak area, Southern Kalimantan, Indonesia.

7 Bronswijk J.J.B. & C.J.Ritsema 1988
Second mission report, modelling component.

8 Toorn A. van den 1988
Report on a laboratory installation and in-service training mission to South Kalimantan.

9 Andriesse, W. 1988
Second Mission report, survey component.

10 Diemont W.H. 1988
Genesis of peats and mineral soils in the Pulau Petak area, Southern Kalimantan.

11 Sevenhuysen, R.J. 1988
Report on the initiation mission of Phase II, water management component.

12 Bronswijk J.J.B., K.Nugroho & A.L.M. van Wijk 1988

Third mission report, modelling component.

13 Andriesse, W. 1988
Third mission report, survey component.

14 Bregt A.K. 1988
Report of the first data processing mission.

15 Sevenhuysen R.J. 1988
Report on the second mission of Phase II, water management component.

16 Mensvoort M.E.F.van 1989
Inventarization, classification and evaluation of (potential) acid sulphate soils ("the survey component")
Report on a general consultancy mission; November 7-18, 1988.

17 Bos M.G. 1989
Report on the third coordination mission.

PLANNING REPORTS

1 Research programme for acid sulphate soils in the humid tropics.
2 Inception report.
3 First progress report.
4 Second progress report.