Analysis of soil chemical composition & physicochemical parameters

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Abstract

Bring human's life on will be the first step of the March odyssey. Well, bring human on mars is already a challenge, but to keep them alive is another one, and probably much more complex. In order to reach this objective, humans who will live on the red planet will have to produce their own food most certainly by agriculture. Unfortunately, Mars soil is completely different from Earth's. Agriculture's areas have to be carefully chosen to avoid spending seeds in a plantation doomed to death because of bad soil. This is why we propose to measure Nitrogen, Phosophorus and Boron (N,P,B) concentration to make sure that soil contains required elements for crops. Nevertheless, physiochemical parameters are also highly decisive. To have better control of crops life and soil viability we will measure soil pH (acidity), but also soil electrical conductivity, which is related to ions concentration of various elements. By measuring all these parameters, we provide strong knowledge of Mars soil composition which will promote agriculture on Martian soil. The aim of this study is twofold: 1) Determination of nitrogen, phosphorus and boron concentration. 2) Measure of soil conductivity and soil pH.

1 Measure of soil salinity

1.1 Principle

Conductivity is the ability of a solution to drive current. It may be measured[1] by applying an alternating electrical current (I) to two electrodes immersed in a solution and measuring the resulting voltage (V). During this process, the cations migrate to the negative electrode, the anions to the positive electrode and the solution acts as an electrical conductor. Ohm's law is used to determine solution resistance (R) and conductivity by knowing the previous parameter:

$$R(\Omega) = \frac{U(V)}{I(A)}.$$

The conductance is defined as

$$G(S) = \frac{1}{R(\Omega)}.$$

Cell constant (K) is defined as the ratio between the distance separating cell electrode (d) and their surfaces (S):

$$K(cm^{-1}) = \frac{d(cm)}{S(cm^2)}.$$

Now, conductivity ($\mathcal{K}$) can be defined as

$$\mathcal{K}(S/cm) = G(S) \cdot K(cm^{-1}).$$

1.2 Material

- Distilled water
- Calibration solution (0.01M KCl solution)

1.3 Procedure

Standard solution preparation. Dissolve 0.7456g KCl in 1 L of water. This solution has a conductivity of 1.41mmhos/cm or dS/m at 25°C.

1.3.1 Soil sample analysis

- Scoop 20g of soil into a large test tube or paper portion cup.
- Add 20mL of distilled water. Periodically stir the suspension and allow it to equilibrate for 15 to 20 minutes. This sample could also be used for a pH measurement after (not before) taking the conductivity measurement.

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[1] Recommended Chemical Soil Test Procedures; North Central Regional Research Publication No. 221 (1998 Revised, PDF corrected 2011)

- Insert the conductivity cell calibrated with the 0.01M KCl into the suspension and read the conductivity in mmhos/cm.

2 Measure of the pH of a soil

2.1 Material

- Beaker of 50ml (one for every sample)
- Balance
- Spatulas
- 5g of soil sample finely grinded (ϕ<2mm)
- Graduated cylinder 50ml
- pH meter
- Standards for calibration

2.2 Procedure

Weight 5g of the gross soil fraction inferior to 2mm in a plastic flask and add 25ml of demineralized water measured with a graduated cylinder. Shake every 20 minutes (3 times in 1 hour) and measure one hour later with a pH meter. If the amount of sample available is very limited, less sample can be used but maintaining always the 1:5 ratio with water.
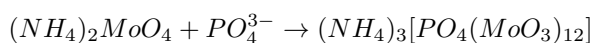
2.3 Remarks

- It is necessary to specify the type of suspension, in this case water, with the code **pH-H$_2$O**.
- The probe needs to always have liquid inside.
- Calibration have to be done with standards of pH 4 and 7.
- It is useful to prepare sample by group of 4, spacing the group within 20 minutes, to be sure of having all the sample measured approximately after the same time since its preparation.

3 Determination of phosphate concentration in a soil

3.1 Principle

Phosphates react with ammonium compound to lead to a colored complex, which absorb light at 840nm: [2]

$$(NH_4)_2MoO_4 + PO_4^{3-} \rightarrow (NH_4)_3[PO_4(MoO_3)_{12}]$$

[2]B. Shyla, Mahadevaiah, G. Nagendrappa ; Spetroc. Acta A. 78, 2011, 497-502

3.2 Material

- Erlenmeyer of 250ml
- Sodium bicarbonate (NaHCO$_3$)
- Filter paper
- Volumetric flasks (250ml, 100ml, 50ml, 25ml, 10ml)
- Graduated pipette
- Beaker of (50ml, 100ml)
- pH paper

3.3 Procedure

Preparation of thiourea solution. A weighed amount, 2g of thiourea is transferred into a 100ml beaker. It is dissolved in about 50ml of water and transferred into a 100ml volumetric flask and diluted to the mark with distilled water.

Preparation of molybdate solution $((NH_4)_2MoO_4)$ A weighed amount, 1.7081g of ammonium molybdate is dissolved in about 150ml of warm water. A slightly milky solution obtained is cooled to room temperature, transferred into a 250ml volumetric flask and diluted to the mark with water.

Preparation of phosphate standard solution A weighed amount, 0.2077g of sodium dihydrogen phosphate (NaH$_2$PO$_4$) is dissolved into a 250ml volumetric flask and diluted to the mark with distilled water. Standard solution is prepared by dilution of the head solution.

Preparation of a soil sample 2.5g of each soil sample are weighed and transferred to a 250ml conical flask. It is shaken with a measured volume, 50ml of sodium bicarbonate (NaHCO$_3$) solution of pH 8.5 and shaked for another 30min. Then it is kept aside for 20-30min to reach the equilibrium. After filtration trough Whatmann filter paper, the clear filtrate is collected in a 50ml volumetric flask and diluted with distilled water. A measured volume , 10ml of the filtrate is transferred into a 50ml beaker an acidified by addition of about 1ml of sulfuric acid solution 0.5M. Then the solution is transferred into a 25ml volumetric flask and diluted to the volume with distilled water. The solution obtained is used for the measure of phosphate content following the procedure described at the paragraph *Soil sample analysis*, section 1.3.
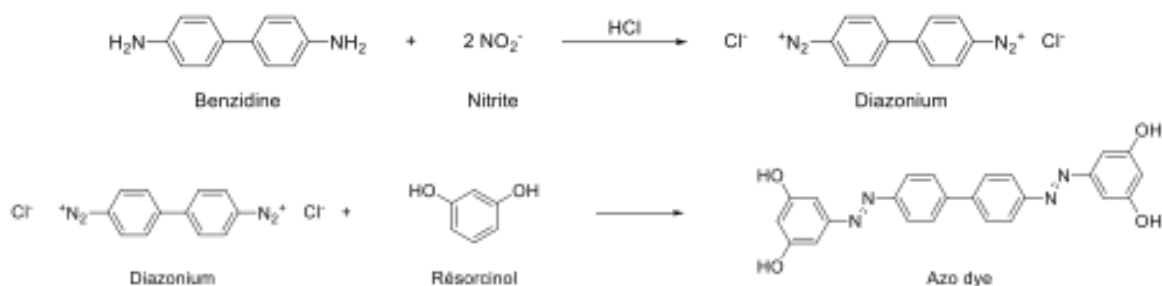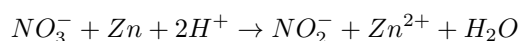
Figure 1: Nitrite determination

Phosphate determination by light absorption Various volumes (0.1 to 2ml) of the working phosphate solution corresponding to 0.5-10 μg.ml^{-1}, 0.5 ml of 5.54×10^{-3} M ammonium molybdate $((NH_4)_2MoO_4)$, 0.5ml of 0.5M sulfuric acid solution (H_2SO_4) and 1ml of 2% thiourea solutions are added into a series of 10ml volumetric flasks. After about 10min the solutions are diluted to the volume with distillated water and the absorbance of theses solutions is read at 840nm against water. Calibration graph is obtained by plotting absorbance values of the solutions against their phosphate concentration.

4 Determination of nitrite and nitrate ions in soil sample

4.1 Principle

Nitrite (NO_2^-) determination In this method[3], benzidine undergoes tetrazotization in the presence of hydrochloric acid, followed by coupling with resorcinol in sodium hydroxide medium to yield orange colored dye. The azo dye formed by benzidine and resorcinol has maximum absorption at 463.5nm against the reagent blank. This is illustrated in Figure 1.

Nitrate (NO_3^-) determination Nitrate cannot be determined directly by this method. A pretreatment is needed to convert nitrate into nitrite and to be able to determine the concentration using the reaction previously described. Nitrate can be reduce into nitrite using zinc in acidic medium according to the following reaction:

$$NO_3^- + Zn + 2H^+ \rightarrow NO_2^- + Zn^{2+} + H_2O$$

By doing the measurement without reducing the nitrates into nitrites, we can determine nitrite concentration. In a second step, when the measurement is done after reducing the nitrate, total concentration in

nitrite and nitrate in determined. A simple calculation allow us to know concentration separately:

$$C_{total} - C_{NO_2^-} = C_{NO_3^-}$$

4.2 Material

- Beaker (25, 50, 100, 250ml)
- Sodium carbonate Na_2CO_3
- Funnel
- Whatman filter paper
- Pipettes (1, 2, 4, 5, 10, 20, 25ml)
- 0.05% Benzidine solution
- HCl 2M
- 5% resorcinol solution
- 2M NaOH
- Spectrophotometer (463.5nm)
- HCl 10.2M
- Zn/NaCl granular mixture
- EDTA 0.0 M
- Sodium fluoride NaF
- 2-mercaptoethanol

4.3 Procedures

Preparation of soil sample for nitrite and nitrate determination. About 1.0g of soil sample is transferred into a clean 50ml beaker. The soil sample is extracted four times with 1% sodium carbonate (Na_2CO_3) using 5 ml each time. Then, the extract is filtered trough Whatman filter paper No. 41. Suitable aliquots of the filtrate are analyzed for nitrate and nitrite determination according to the following procedures.

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[3]Nagaraj P., Gopalakrishna Bhat N., Chandrashekara KG.; Int. J. Chem Sud. 2016; 4(3), 101-105

Nitrite determination Aliquots of the solution, containing 5 to 70μg of nitrite are pipetted out into 25ml standard flasks, each containing 1ml of 0.05% benzidine and 1ml of 2M hydrochloric acid solutions. The solutions in each standard flask were mixed well and set aside for 3 to 4 minutes to allow the completion of tetrazotization reaction with occasional mixing. Then, 2ml of 5% resorcinol and 2ml of 2M sodium hydroxide solutions are added to each standard flask. Light orange colour is developed. The content of each standard flask is diluted up to the mark using distilled water. Then, the absorbance is measured at 463.5nm against reagent blank. The nitrite content in the aliquot sample is determined using a calibration curve.

Nitrate determination Nitrate stock solution of volume 10ml is transferred into a beaker containing 5ml of 10.2M hydrochloric acid and 5g of Zn/NaCl granular mixture. The content is allowed to stand for 15min with occasional shaking. Nitrate is reduced into nitrite. Then the solution is filtered trough Whatman filter paper No.41 into a 100ml standard flask. Then aliquots of the solution, containing 5 to 70μg of reduced nitrate are pipetted out and determination is carried out as in the case of nitrite.

Remarks Fe^{3+} and Cu^{2+} interfere with the measurement of NO_2^- and NO_3^- if their concentration are superior to the tolerance limit:
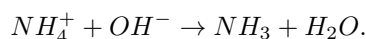
Ion	Tolerance limit ($\mu g \cdot cm^{-3}$)
$Fe^{3}+$	70
$Cu^{2}+$	80

The effect of Fe^{3+} and Cu^{2+} can be masked by using sodium fluorid (NaF) and 2-mercaptoethanol respectively. To avoid interference, of other metal ions, 3ml of EDTA 0.02M solution can be added.

5 Determination of ammonium in soil samples

5.1 Principle

The principle[4] of ammonium determination is based on the fact that the ammonia ion is released as amomonia gas upon addition of excess caustic soda (NaOH).

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O.$$

The use of a ion-selective electrode enables measurement of ammonia content which is directly related to the ammonium content. The outer membrane of the

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[4]Metrohm, Application bulletin n°132/2, Determination of ammonium with the ion-selective electrode

electrode allows the ammonia to diffuse through. The change of pH value of the inner electrolyte solution is monitored by a combined glass electrode.

5.2 Material

- pH/ion meter
- Magnetic stirrer
- NH_3 specific electrode
- Temperature sensor
- HCl 2mol/L
- NaOH 10mol/L
- Standard solution of NH_4Cl
- Conditioning solution of NH_4Cl 0.1mol/L
- Burette
- Erlenmeyer
- 5 standard flasks (100ml)

5.3 Procedure

Sample preparation. After weighing, the soil sample is dried and then boiled for 1 hour in HCl (2mol/L) The solution is filtered and the volume to be pipetted is adjusted to pH 12 with NaOH.

Measure of ammonium content. After the addition of NaOH the pH-value must be at least 12. Acidic samples must be neutralized before the addition of NaOH. Add the NaOH and begin the measurement immediately.

The electrode is just put in sample which is stirred and the the value is recorded on the device when the value becomes stable.

A calibration curve is built by using a range of standard concentration in according to sample concentration.

6 Boron determination in soil samples by azomethine-H method

6.1 Principle

The Azomethine-H Method involves the coupling of H-acid with an aromatic hydroxyaldehyde, such as salicylaldehyde, due to the catalytic effect when boron is present. At neutral pH values and a controlled temperature, the condensation reaction is quickly completed (within 15 minutes). After product formation, the solution is adjusted to an acidic pH for optimum color
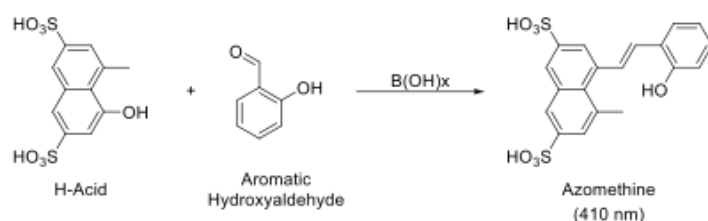
Figure 2: Boron determination in soil samples

measurement at 410nm (yellow) using a colorimeter or spectrophotometer. This is illustrated in *Figure 2*.

6.2 Material

- Plastic flask
- Spectrophotometer
- Plasticware
- Whatman No.42 filter paper
- Ammonium acetate (CH_3COONH_4), 500g
- EDTA disodium salt, 50g
- Glacial acetic acid
- Azomethine-H, 3g
- L-Ascorbic acid solution
- Boron stock solution 1000ppm
- Standard flasks
- Activated carbon
- Pipette (1, 2, 3, 4, 5ml)
- EDTA 0.2M solution (for Fe, Al, Cu, interference)[5]

6.3 Procedure

Soil sample determination

- Scoop 10cm^3 or weigh 10g of air-dried, sieved soil into a low boiling flask capable of use with a water-reflux condensing apparatus.
- Add 20mL of Boron extracting solution to the flask.
- Use small plastic funnels as condensers, weigh the flask with soil and extracting solution (without funnel) to 0.01g and record the weight on the flask. Place the funnel on the flask before heating.

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[5] J. Rubb. Res. Inst. Malaysia, 1984, 32(3), 182 -190

- Remove the funnel and immediately place the flask with soil and extracting solution on a balance and add hot deionized water to attain original recorded weight. Swirl to mix.

- Filter the suspension, while still warm, through Whatman No.42 filter paper, catching the filtrate in plastic sample bottles.

- Inspect supernatant solution or filtrate for clarity and refilter if necessary. For colorimetric B analysis: if the filtrate is yellow in color, refilter with < 1/8 teaspoon of activated charcoal in the filter paper cone (McGeehan et. al., 1989).

Solutions preparation *Boron extracting solution, (CaCl$_2$ 10mM):* Dissolve 1.5g of CaCl$_2$· 2H$_2$O in a 1 L volumetric flask containing 600mL of deionized water. Fill to the volume with deionized water and mix thoroughly.

Buffer-masking Solution: Dissolve 250g of ammonium acetate and 15g of ethylenedinitrilo-tetraacetic acid disodium salt (i.e., disodium ethylenediamine tetraacetate, EDTA disodiumsalt) in 400mL of high-quality, deionized water and slowly add 125mL of glacial acetic acid.

Azomethine-H Solution: Dissolve 0.45g of Azomethine-H in 100mL of 1% L-ascorbic acid solution. Prepare fresh reagent each week and store in the refrigerator.

Boron Stock Solution (1,000ppm B): Weigh 5.716g boric acid (H$_3$BO$_3$) into a 1L volumetric flask and dilute to volume with deionized water.

Boron Stock Solution (20 ppm B): Pipet 20mL of 1,000ppm B solution into 1,000mL volumetric flask and dilute to volume with deionized water.

Working Standards: Pipet the appropriate volumes (see Table 1) of 20ppm B into 100mL volumetric flasks and dilute to volume with deionized water.

Beaker	V. of 20ppm Boron std. mL	Boron final vol. mL	Boron in solution ppm	Boron in soil mg/Kg
1	0	100	0	0
2	1	100	0.2	0.4
3	2	100	0.4	0.8
4	4	100	0.8	1.6
5	5	100	1.6	3.2

Table 1: Working standards.

Boron determination

- If necessary, filter supernatant solution through Whatman No.42 filter paper (or similar grade paper) fitted in plastic funnels. Inspect filtrate for clarity and refilter if necessary. If filtrate is strongly yellow, refilter with one-half teaspoon of activated charcoal in the filter paper cone.

- Pipet a 1mL aliquot of soil extract into a plastic tube or small beaker, followed by mL of the buffer-masking solution. Thoroughly mix by swirling.

- Add 2mL of Azomethine-H reagent and mix the contents thoroughly.

- Allow mixture to stand 30 minutes, then measure light transmission at 420nm wavelength.

- Prepare a standard curve by adding 1mL of each of the B working standards (Table 2) to a plastic tube or beaker and follow steps 2 through 4 as applied to soil extracts. Plot percentage transmittancy versus B concentration

7 Determination of soil texture

This part of the experiment is illustrated in *Figure 3*.

8 Statistical method for collecting soil samples
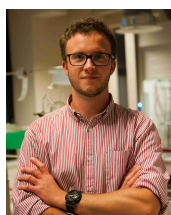
8.1 Principle

To get representative measures of pH and concentration of different elements, it is required to use sampling method.

The rectangle area of measurement is split into 5 parts on a side and 4 on the other one, as illustrated in *Figure 4*. On the center of each small rectangle, a sample is taken. It is important to note that every sampling place have to be spaced of 2m. Sample on a line (side of 4 rectangles) are mixed and the measurement is performed as described in the previous part of this paper. The final value is obtained by calculating the average on all measurement. The accuracy can be improved by reading 3 times the sample after his preparation in agreement with the described method.

This method has to be followed for each ground layer that constitute a different type of soil.

About the author

Maximilien Richald got his degree of chemical engineering at Meurice institute in Brussels in 2015. For two years, he has been doing a Phd in chemical synthesis at the Université catholique de Louvain. Maximilien already had the opportunity to work several times in pharmaceutical companies, in research departments and also in catalysis. These professional experiences gave him tools to deal with differents fields of science and provided him strong scientific knowledge. Furthemore, he worked abroad during 7 months where he was trained to manage a team and brought a project to life. All of these experiences prepared him to lead this mission to success.

Determining Soil Texture by the "Feel Method"

Texture Classification
C = Coarse
MC = Moderately Coarse
M = Medium
F = Fine

Start

Place approximately one tablespoon of soil in palm. Add water a drop at a time and knead the soil to break down all aggregates. Soil is at the proper consistency when plastic and mobile, like moist putty.

Add dry soil to soak up water.

Does soil remain in a ball when squeezed? — NO → Is the soil too dry? — YES (up)

Is the soil too wet? — YES (up to add dry soil)

NO → SAND C*
0-10% **

YES (down) →

Place ball of soil between thumb and forefinger, gently pushing the soil with the thumb, working it upward into a ribbon. Form a ribbon of uniform thickness and width. Allow the ribbon to emerge and extend over the forefinger, breaking from its own weight.

Does the soil form a ribbon? — NO → LOAMY SAND C*
0-15% **

YES (down)

Does the soil make a weak ribbon less than 1" long before breaking? — NO → Does the soil make a medium ribbon 1" to 2" long before breaking? — NO → Does the soil make a strong ribbon 2" or longer before breaking?

Column 1 (YES):
Excessively wet a small pinch of soil in palm of hand and rub with forefinger.

Sandy Loam MC 0-20% ← YES — Does the soil feel very gritty?
NO ↓
Silt or Silt Loam M 0-27% ← YES — Does the soil feel very smooth?
NO ↓
Loam M 7-27% ← YES — Neither grittiness nor smoothness predominates.

Column 2 (YES):
Excessively wet a small pinch of soil in palm of hand and rub with forefinger.

Sandy Clay Loam MC 20-35% ← YES — Does the soil feel very gritty?
NO ↓
Silty Clay Loam F 27-40% ← YES — Does the soil feel very smooth?
NO ↓
Clay Loam F 27-40% ← YES — Neither grittiness nor smoothness predominates.

Column 3 (YES):
Excessively wet a small pinch of soil in palm of hand and rub with forefinger.

Sandy Clay MC 35-55% ← YES — Does the soil feel very gritty?
NO ↓
Silty Clay F 40-60% ← YES — Does the soil feel very smooth?
NO ↓
Clay F 40-100% ← YES — Neither grittiness nor smoothness predominates.

* Sand Particle size should be estimated (very fine, fine, medium, coarse) for those textures. Individual grains of very fine sand are not visible without magnification and there is a gritty feeling to a very small sample ground between the teeth. Some fine sand particles may be just visible. Medium sand particles are easily visible. Examples of sand size descriptions where one size is predominant are; very fine sand, fine sandy loam, loamy coarse sand.

** Clay percentage range.

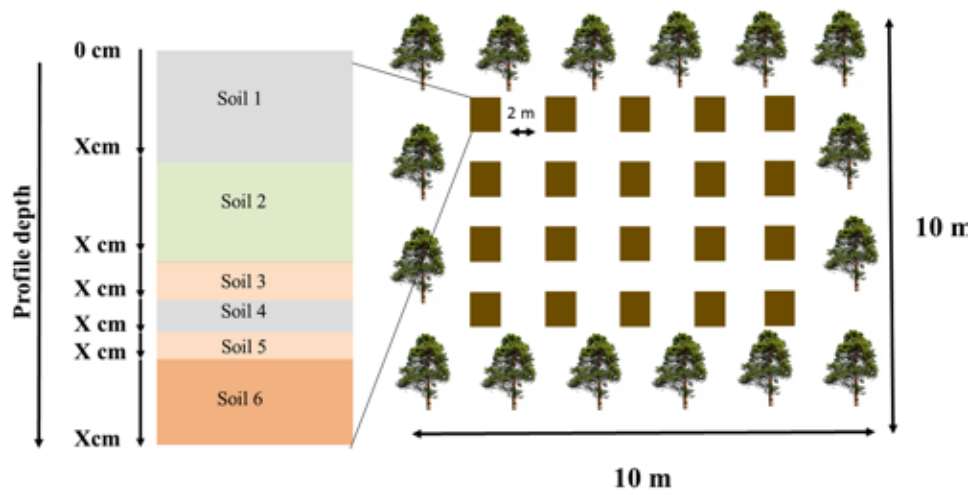Modified from: Thien, Steven J., Kansas state University, 1979 Jour. Agronomy education.

Figure 3: Determination of soil texture.

Figure 4: Soil collection.