Water Content and Loss on Ignition

1.1 Introduction

Schematically, a soil is made up of a solid, mineral and organic phase, a liquid phase and a gas phase. The physical and chemical characteristics of the solid phase result in both marked variability of water contents and a varying degree of resistance to the elimination of moisture.

For all soil analytical studies, the analyst must know the exact quantity of the solid phase in order to transcribe his results in a stable and reproducible form. The liquid phase must be separate, and this operation must not modify the solid matrix significantly (structural water is related to the crystal lattice).

Many definitions exist for the terms "moisture" and "dry soil". The water that is eliminated by moderate heating, or extracted using solvents, represents only one part of total moisture, known as hygroscopic water, which is composed of (1) the water of adsorption retained on the surface of solids by physical absorption (forces of van der Waals), or by chemisorption, (2) the water of capillarity and swelling and (3) the hygrometrical water of the gas fraction of the soil (ratio of the effective pressure of the water vapour to maximum pressure). The limits between these different types of water are not strict.

"Air-dried" soil, which is used as the reference for soil preparation in the laboratory, contains varying amounts of water which depend in particular on the nature of secondary minerals, but also on external forces (temperature, the relative humidity of the air). Some andisols or histosols that are air dried for a period of 6 months can still contain 60% of water in comparison with soils dried at 105°C, and this can lead to unacceptable errors if the analytical results are not compared with a more realistic

reference for moisture.[1] Saline soils can also cause problems because of the presence of hygroscopic salts.

It is possible to determine remarkable water contents involving fields of force of retention that are sufficiently reproducible and representative (Table 1.1). These values can be represented in the form of capillary potential (pF), the decimal logarithm of the pressure in millibars needed to bring a sample to a given water content (Table 1.1). It should be noted that because of the forces of van der Waals, there can be differences in state, but not in form, between water likely to evaporate at 20°C and water that does not freeze at –78°C. The analyst defines remarkable points for example:

– *The water holding capacity*, water content where the pressure component of the total potential becomes more significant than the gravitating component; this depends on the texture and the nature of the mineral and approaches *field capacity* which, after suitable drainage, corresponds to a null gravitating flow.

– *The capillary frangible point*, a state of moisture where the continuous water film becomes monomolecular and breaks.

– *The points of temporary and permanent wilting* where the pellicular water retained by the bonding strength balances with osmotic pressure; in this case, except for some halophilous plants, the majority of plants can no longer absorb the water that may still be present in the soil.

– *The hygroscopic water* which cannot be easily eliminated in the natural environment as this requires considerable energy, hygroscopic water evaporates at temperatures above 100°C and does not freeze at –78°C.

– *The water of constitution* and hydration of the mineral molecules can only be eliminated at very high pressures or at high temperatures, with irreversible modification or destruction of the crystal lattice.

These types of water are estimated using different types of measurements to study the water dynamics and the mechanisms related to the mechanical properties of soils in agronomy and agricultural engineering, for example:

– usable reserves (UR), easily usable reserves (EUR), or reserves that are easily available in soil–water–plant relations.

– thresholds of plasticity, adhesiveness, liquidity (limits of Atterberg, etc.).

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[1] It should be noted that for these types of soil, errors are still amplified by the ponderal expression (because of an apparent density that is able to reach 0.3) this is likely to make the analytical results unsuitable for agronomic studies.
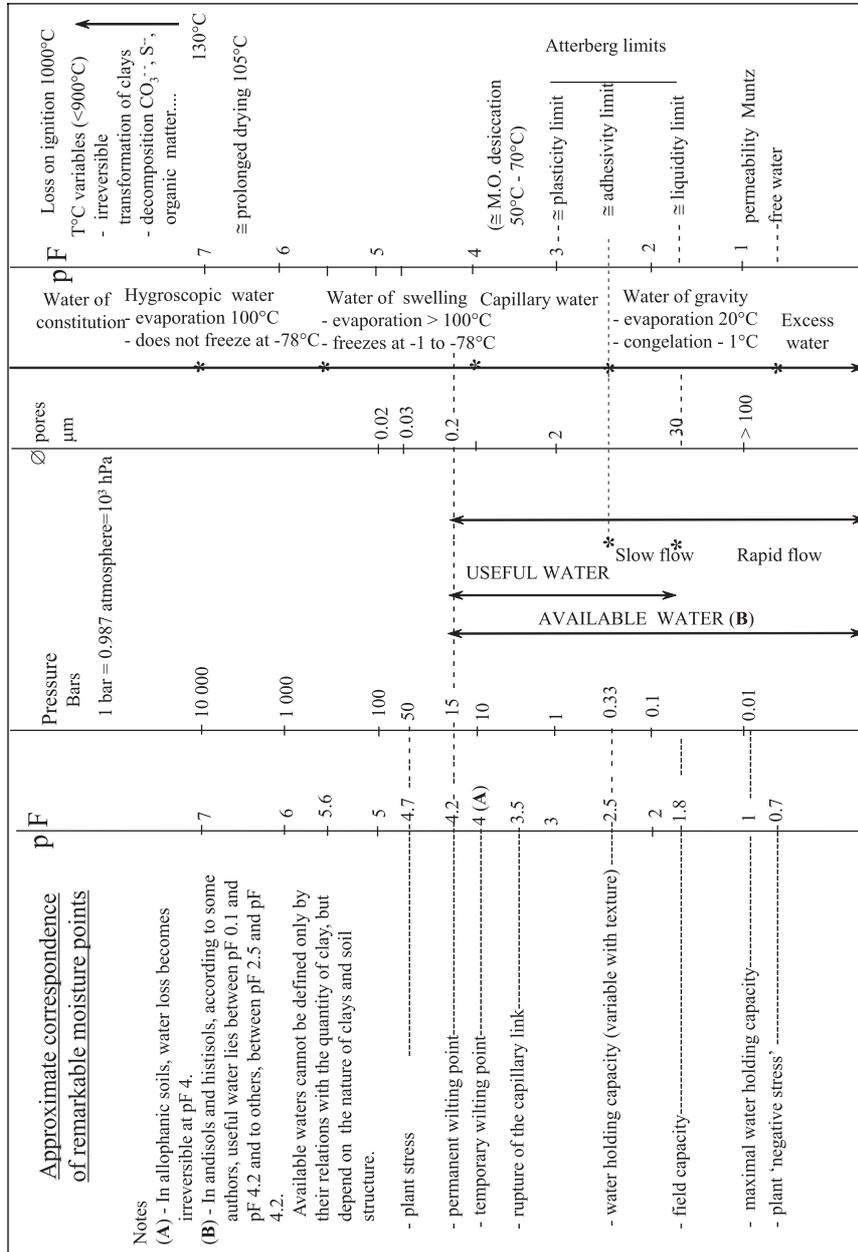
Table 1.1 - Approximate correspondence moistures – pressure – diameter of the pores – types of water and critical points in soils with respect to plant requirements

<u>Approximate correspondence of remarkable moisture points</u>

Notes

(A) - In allophanic soils, water loss becomes irreversible at pF 4.

(B) - In andisols and histisols, according to some authors, useful water lies between pF 0.1 and pF 4.2 and to others, between pF 2.5 and pF 4.2.

Available waters cannot be defined only by their relations with the quantity of clay, but depend on the nature of clays and soil structure.

pF	Pressure Bars (1 bar = 0.987 atmosphere = 10³ hPa)	Critical points	Ø pores μm	Types of water	pF	Loss on ignition 1000°C — T°C variables (<900°C), irreversible transformation of clays, decomposition CO₃⁻⁻, S⁻, organic matter...
7	10 000			Water of constitution	7	130°C
6	1 000			Hygroscopic water — evaporation 100°C — does not freeze at -78°C	6	≅ prolonged drying 105°C
5.6						
5	100				5	
4.7	50	- plant stress	0.02 / 0.03	Water of swelling — evaporation > 100°C — freezes at -1 to -78°C		
4.2	15	- permanent wilting point	0.2		4	(≅ M.O. desiccation 50°C - 70°C)
4 (A)	10	- temporary wilting point		Capillary water		
3.5		- rupture of the capillary link			3	≅ plasticity limit
3	1		2			≅ adhesivity limit
2.5	0.33	- water holding capacity (variable with texture)		Water of gravity — evaporation 20°C — congelation - 1°C	2	≅ liquidity limit
2	0.1					
1.8		- field capacity	30			
1	0.01	- maximal water holding capacity	> 100	Excess water	1	permeability Muntz — free water
0.7		- plant 'negative stress'				

Atterberg limits

USEFUL WATER

AVAILABLE WATER (B)

Slow flow — Rapid flow

This brief summary gives an indication of the complexity of the concept of soil moisture and the difficulty for the analyst to find a scientifically defined basis for dry soil where the balance of the solid, liquid and gas phases is constant.

1.2 Water Content at 105°C (H_2O^-)

1.2.1 Principle

By convention, the term "moisture" is considered to be unequivocal. Measurement is carried out by gravimetry after drying at a maximum temperature of 105°C. This increase in temperature maintained for a controlled period of time, is sufficiently high to eliminate "free" forms of water and sufficiently low not to cause a significant loss of organic matter and unstable salts by volatilization. Repeatability and reproducibility are satisfactory in the majority of soils if procedures are rigorously respected.

1.2.2 Materials

– 50 × 30 mm borosilicate glass low form weighing bottle with ground flat top cap.
– Vacuum type Ø 200 mm desiccator made of borosilicate glass with removable porcelain floor, filled with anhydrous magnesium perchlorate [$Mg(ClO_4)_2$].
– Thermostatically controlled drying oven with constant speed blower for air circulation and exhausting through a vent in the top of oven – temperature uniformity ± 0.5–1°C.
– Analytical balance: precision 0.1 mg, range 100 g.

1.2.3 Sample

It is essential to measure water content on the same batch of samples prepared at the same time (fine earth with 2 mm particles or ground soil) for subsequent analyses. It should be noted that the moisture content of the prepared soil may change during storage (fluctuations in air moisture and temperature, oxidation of organic matter, loss or fixing of volatile substances, etc.).

This method can be considered "destructive" for certain types of soils and analyses, as the physical and chemical properties can be transformed. Samples dried at 105°C should generally not be used for other measurements.

1.2.4 Procedure

– Dry tared weighing bottles for 2 h at 105°C, let them cool in the desiccator and weigh the tare with the lid placed underneath: m_0
– Place about 5 g of air-dried soil (fine earth sieved through a 2 mm mesh) in the tare box and note the new weight: m_1
– Place the weighing bottles with their flat caps placed underneath in a ventilated drying oven for 4 h at 105°C (the air exit must be open and the drying oven should not be overloaded)
– Cool in the desiccator and weigh (all the lids of the series contained in the desiccator should be closed to avoid moisture input): m_2
– Again place the opened weighing bottles in the drying oven for 1 h at 105°C and weigh under the same conditions; the weight should be constant; if not, continue drying the weighing bottles until their weight is constant

$$\% \text{ water content at } 105°C = 100 \times \frac{m_1 - m_2}{m_1 - m_0}.$$

1.2.5 Remarks

The results can also be expressed in pedological terms of water holding capacity (HC) by the soil: $\text{HC} = 100 \times \dfrac{m_1 - m_2}{m_2 - m_0}.$

The point of measurement at 105°C with constant mass is empirical (Fig. 1.1). A temperature of 130°C makes it possible to release almost all "interstitial water", but this occurs to the detriment of the stability of organic matter. The speed of drying should be a function of the temperature, the surface of diffusion, the division of the solid, ventilation, pressure (vacuum), etc.

Respecting the procedure is thus essential:
– For andisols and histosols, the initial weighing should be systematically carried out after 6 h.
– For saline soils with large quantities of dissolved salts, the sample can be dried directly, soluble salts then being integrated into the "dry soil" or eliminated beforehand by treatment with water.

Fig. 1.1 - Theoretical diagrammatic curve showing water moved at a given temperature as a function of time (180°C = end of H_2O losses in allophanes)
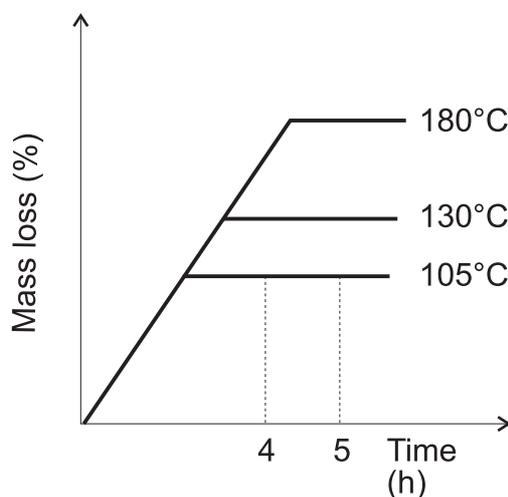
## 1.3 Loss on Ignition at 1,000°C (H_2O^+)

1.3.1 Introduction

As we have just seen, the reference temperature (105°C) selected for the determination of the moisture content of a "dry soil" represents only a totally hypothetical state of the water that is normally referred to as H_2O^-.

When a sample undergoes controlled heating and the uninterrupted ponderal variations are measured, curves of "dehydration" are obtained whose inflections characterize losses in mass at certain critical temperatures (TGA).[1] If one observes the temperature curve compared to a thermically inert substance (Fig. 1.2), it is possible to determine changes in energy between the sample studied and the reference substance, this results in a change in the temperature which can be measured (DTA–DSC).[2]

– If the temperature decreases compared to the reference, an endothermic peak appears that characterizes loss of H_2O (dehydration), of OH^- (dehydroxylation), sublimation, or evaporation, or decomposition of certain substances, etc.

– If the temperature increases compared to the reference, an exothermic peak appears that characterizes transformations of crystalline structures, oxidations ($Fe^{2+} \rightarrow Fe^{3+}$), etc.

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[2] *TGA* thermogravimetric analysis; *DTA* differential thermal analysis; *DSA* differential scanning calorimetry (cf. Chap. 7).

Fig. 1.2 - Schematized example of thermal analysis curves TGA (*solid line*) and DTA (*dashed line*)
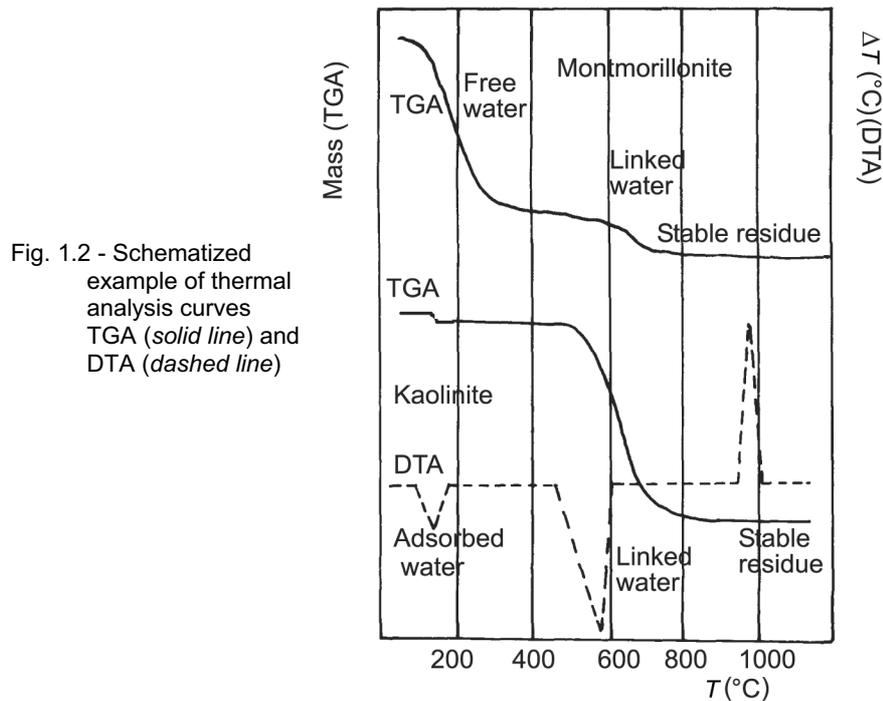
The simultaneous analysis of the gases or vapours that are emitted and X-ray diffraction (cf. Chap. 4) of the modifications in structure make it possible to validate the inflections of the curves or the different endo- and exothermic peaks.

As can be seen in the highly simplified Table 1.2, the most commonly observed clays are completely dehydroxyled at 1,000°C, oxides at 400°C or 500°C, carbonates, halogens, sulphates, sulphides are broken down or dehydrated between 300°C and 1,000°C, and free or bound organic matter between 300°C and 500°C. The temperature of 1,000°C can thus be retained as a stable reference temperature for loss on ignition, the thermal spectra then being practically flat up to the peaks of fusion which generally only appear at temperatures higher than 1,500°C or even 2,500°C.

1.3.2 Principle

The sample should be gradually heated in oxidizing medium to 1,000°C and maintained at this temperature for 4 h.

Table 1.2 Dehydration and dehydroxylation of some clays, oxides and
salts as a function of temperature in °C

type	name	dehydration[a]	dehydroxylation[b]
clays 1:1	Kaolinite–halloysite	350	1,000
clays 2:1	smectites – montmorillonite	370	1,000
clays 2:1	Illite – micas	350–370	1,000
clays 2:1	vermiculite	700	1,000
clays 2:1:1	chlorite	600	800
fibrous clays	Sepiolite–palygorskite	300	800–900
	allophane	200	900–1,000
iron oxides	Hematite α Fe_2O_3	(flat spectrum)	1,000
	goethite α FeO–OH	100	370
	magnetite Fe_2O_3	375	650
Al oxides	gibbsite γ-$Al(OH)_3$	100	350
Ca carbonate	Calcite–aragonite $CaCO_3$	–	950–1,000
Mg carbonate	magnesite $MgCO_3$	–	710
Ca–Mg carbonate	dolomie $CaMg(CO_3)_2$	–	800–940
halogenous compounds	sodium chloride NaCl	–	800 (fusion)
sulphate	gypsum $CaSO_4$, $2H_2O$	–	300
sulphide	pyrite FeS_2	–	615
organic compounds	free or linked organic matter	–	300–500

[a] Dehydration: loss of water adsorbed on outer or inner surfaces, with or without reversible change in the lattice depending on the types of clay, water organized in monomolecular film on surface oxygen atoms or around exchangeable cations.

[b] dehydroxylation (+ decarbonatation and desulphurization reactions), loss of water linked to lattice (OH^-), irreversible reaction or destruction of the structure, water present in the cavities, O forming the base of the tetrahedrons.

Loss on ignition is determined by gravimetry. It includes combined water linked to the crystal lattice plus a little residual non-structural adsorbed water, organic matter, possibly volatile soluble salts (F^-, S^{2-}) and carbonates (CO_3^{2-}, CO_2). The use of an oxidizing atmosphere is essential to ensure combustion of the organic matter and in particular oxidation of reduced forms of iron, this being accompanied by an increase in mass of the soils with minerals rich in Fe^{2+}. A complete analysis generally includes successive measurements of H_2O^- and H_2O^+ on the same sample.

1.3.3 Equipment

– Platinum or Inconel (Ni–Cr–Fe) crucible with cover, diameter 46 mm.
– Analytical balances (id. H_2O^-)
– Desiccator (id. H_2O^-)
– Muffle electric furnace (range 100–1,100°C) with proportional electronic regulation allowing modulation of the impulses with oscillation of about 1°C around the point of instruction; built-in ventilation system for evacuation of smoke and vapour
– Thermal protective gloves
– 300 mm crucible tong

1.3.4 Procedure

– Tare a crucible, heat it to 1,000°C and cool it in the desiccator with its lid on: m_0
– Introduce 2–3 g of air-dried soil crushed to 0.1 mm: m_1
– Dry in the drying oven at 105°C for 4 h
– Cool in the desiccator and weigh: m_2
– Adjust the lid of the crucible so it covers approximately 2/3 of the crucible and put it in the electric furnace
– Programme a heating gradient of approximately 6°C per minute with a 20-min stage at 300°C, then a fast rise at full power up to 1,000°C with a 4-h graduation step (the door of the furnace should only be closed after complete combustion of the organic matter)
– Cool the crucible in the desiccator and weigh: m_3

1.3.5 Calculations

$m_1 - m_0 =$ weight of air-dried soil
$m_1 - m_2 =$ moisture at 105°C

$m_2 - m_0 =$ weight of soil dried at 105°C

$m_2 - m_3 =$ loss on ignition

$$H_2O^-\% = 100 \times \frac{m_1 - m_2}{m_1 - m_0}$$ related to air-dried soil

$$H_2O^+\% = 100 \times \frac{m_2 - m_3}{m_2 - m_0}$$ related to soil dried at 105°C

1.3.6 Remarks

Knowing the moisture of the air-dried soil, it is possible to calculate the weight of air-dried soil required to work with a standard weight soil dried at 105°C, thus simplifying calculations during analyses of the samples.

To obtain the equivalent of 1 g of soil dried at 105°C, it is necessary to weigh:

$$\frac{100}{100 - wc}$$ with $wc = \%$ water content of air dried soil.

Platinum crucibles are very expensive and are somewhat volatile at 1,000°C, which means they have to be tared before each operation, particularly when operating in reducing conditions.

Combustion of organic matter with insufficient oxygen can lead to the formation of carbide of Pt, sulphides combine with Pt, chlorine attacks Pt, etc.

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