

SOME PROBLEMS IN
ANALYSIS OF SOILS IN ARID AREAS

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Analysis of soils of arid zones presents, in addition to the difficulties usually encountered, some peculiar sources of inaccuracy. Various chemical and physical factors, almost all of them due to more or less soluble salts, interact to affect the final value. In addition to inaccuracy, interferences may take two forms: chemical interference due to solubility of salts or physical interference due to more or less crystallized forms of sparingly soluble salts. The first type is found each time soil is brought into contact with an aqueous solution, i.e. during all chemical analysis of soils. The second type of interference is found when calcium carbonate and gypsum are major components of the soil. Analysis of their physical parameters give different results whether these salts react as soluble or insoluble particles.

The following paper proposes to list the difficulties specific to analysis of arid soils. General problems are reviewed and practical examples are shown on two soil samples. Only basic determinations are considered.

MATERIALS

Two characteristic arid soils have been analyzed in a collaborative study by eighteen laboratories. Sixteen of them are central laboratories of soil survey in their own country. All but two belong to states which are members of ACSAD, and they perform routine work rather than research.

The first soil sample (Soil A) has been sampled in the surface horizon

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described as Camborthic Xerathic Holomorphic (ILAIWI). Soil B belongs to a similar profile where gypsum accumulation is visible as small crystals. Sampling has been done in the gypsum accumulation zone between 40 and 65 cm. Main characteristics are given in Table 1. The collaborative study included water and plant analysis not mentioned in this paper.

Table 1. Data on soil samples A and B.

Fraction (%)	Clay	Silt	Sand	CaCO ₃	SP	pH	OM%	N%	
Soil A	37	27	34	21.3	64	8.0	0.8	0.13	
Soil B	43	30	24	18.4	78	8.1	0.1	0.04	
meq/l ⁻¹	Ca	Mg	K	Na	Cl	SO ₄	HCO ₃	pH	EC
Sat. ext. A	8	5.3	0.4	4.8	5.8	8	5.3	7.8	1.7
Sat. ext. B	31	26	0.8	130	96	92	1.6	7.6	16.6
Analysis	C.E.C. meq/100 g	Exch. Na meq/100 g	P(Olsen) ppm	Gyps. %	H ₂ O 15 bar	H ₂ O % 1/3 bar			
Soil A	19	3.7	10	0	16.8	24.1			
Soil B	20	6.5	-	10.8	-	-			

METHODS

No specific recommendations have been made for using special methods; soil samples A and B have been analyzed by methods used for routine determinations of soil parameters in each laboratory. All the results of soil A are expressed 105°C dry basis and soil B on air-dry basis.

1. Most laboratories used the same type of method for almost all the determinations.
2. Procedures are different: a typical example is the cation exchange capacity done by each laboratory using ammonium acetate as a saturating solution and sodium acetate as a displacing solution. Procedures may include washing step, correction for soluble salts, etc.... The overall process is so different that each laboratory may be considered to use a different method. It was not possible

to investigate in detail the modifications adopted by each one. Nevertheless, the need to modify a proposed procedure is a clear sign of the potential difficulties of analysis of arid soils. There is no wonder, then, to find a wide variation of results around the mean value. Implications of these variations are twofold: (1) They must be considered when compiling results from files without a practical possibility of redoing them (survey at regional level for instance), (2) Precision of result must comply with analytical requirements of classification systems. The consequences are particularly important in U.S. Soil Taxonomy which relies on very precise analytical limits.

CRITERIA FOR EVALUATION OF RESULTS

Twenty sub-samples drawn from A and B respectively have been tested for homogeneity by analyzing their total sand content. Relative standard deviation for $n=20$ is 5% for A and 6% for B. If we assume that many properties are proportional to particle size we may consider 5% as the lowest possible relative standard deviation (for $n=20$) representing the utmost compatible with sample homogeneity.

On this basis we consider in this paper (for $n=10$):

- an r.s.d. less than 10% as excellent.
- an r.s.d. lying between 10-20% as good.
- an r.s.d. between 20 and 30 as poor.
- an r.s.d. exceeding 30% as questionable.

Of course these values are quite arbitrary, but r.s.d. value is a convenient criterion for evaluating precision. Evaluation of accuracy is estimated by a different approach not considered in this paper.

For each determination, the potential sources of errors are listed and practical examples are discussed on results of A and B samples.

PARTICLE SIZE DISTRIBUTION, SOURCES OF ERRORS

Procedures include pipette (Piper, 1942), hydrometer (Day, 1950), plumet (Marschall, 1956). All methods are based on Stokes' law application and in all cases the first source of misunderstanding lies in the definition of particle. In arid soils we must agree on whether calcium carbonate and gypsum are comprehended as particles or not: On the one hand noting such calcium sulfate dihydrate appears in the words clay, silt and sand; On the other, in solution a crystal of gypsum is likely to follow Stokes' law more closely than an aggregate of real clay which may be counted as fine sand. Significant differences at this level are displayed in Table 2 for soil A.

Table 2. Effect of calcium carbonate removal on expression of results:
Soil A.

CaCO ₃ %	Clay (1)	Silt (2)	Sand (3)	(1) + (2) + (3)	CaCO ₃ status
21.3	37	27	34	98	a. Not removed
21.3	32	15	28	75	b. Removed

In line a calcium carbonate is accounted for in clay, silt and sand fraction and again as calcium carbonate. This way of expressing results, though being the most common one, is misleading. Furthermore it does not give any information on the size of CaCO₃ particles though it is an important aspect. Line b presents data nearer to reality. Comparison of lines a and b shows that calcium carbonate is mainly silt-sized in our sample.

This preliminary source of imprecision being cleared up, the main sources of problems are due to:

- a. Inappropriate dispersion of the sample;
- b. Deviations from theoretical conditions in which Stokes' law applies;
and
- c. Imperfect sampling of suspension or errors during weighting
(pipette method).

Accumulation of these errors leads to a wider variation between labora-

tories than between methods, a relative standard variation of 6% for pipette and for plummet method as well, being claimed for a sample having 28% clay (Bannister et al., 1973). Dispersion method has no effect in itself as shown in Table 3.

Table 3. Dispersion method and precision of clay percentage (from Edwards and Brenner, 1967; soil data: pH 7.8; CaCO₃ 26.5%; Org. carb. 0.35%).

Dispersion method	Ultra-sonic	Na-Polyphos.	Resin	Na-Hypo-bromite
Clay %	25	24.3	26.4	22.7

In conclusion, for soils containing soluble salts, if we assume a proper dispersion, regardless the method used, the most insidious errors are due to deviations from Stokes' law caused by:

- a. Change in viscosity of solution due to salt dissolution or temperature variation during the experiment;
- b. Partial flocculation due to excess of double charged particles;
- c. Change in time of sedimenting and/or depth of sampling because of different density of particles (Table 4), not to mention surface tension effect, and nonsphericity of particles greater than 5 micros in diameter, all features inherent to the complex nature of soils and not distinctive of arid ones.

These effects are felt differently by each method. Variation of density affects the hydrometer method more than the pipette method and the clay fraction (and silt) more than sand.

Table 4. Deviation from Stokes' law: effect of density.

Real density	Error	Material	Effect on clay fraction
2.2	+33.3	Montmorillonite (d=2.3) Vermiculite (d=2.32)	Overestimation
2.4	+14.1	Gypsum (d=2.32)	No
2.65	0		No
2.80	-11.1	Calcite, dolomite	Underestimation
2.90	-15.8		Underestimation

COMMENTS ON RESULTS ON SOILS A AND B

Results are shown in Tables 5 and 6. As expected, precision is poorer for clay and silt fractions than for sand, the variation being more important for sample B (14% gypsum) than for A (gypsum-free). Total sand is determined better than subfractions which are affected by sieving errors. Since repeated washing is necessary to separate total sand, most errors may be avoided by choosing a sedimentation time slightly longer than requested. The 30% r.s.d. for sample B sand is probably due to loss of crystallization water during drying and partial dissolution of gypsum solution.

Table 5. Sample A: Results of particle size distribution (n = 12).
(Results expressed on 105°C basis; 80% of the results are obtained by pipette method.)

Fraction	Clay	Silt	Total sand	Fine sand	Medium
Range	14-46	42-19	44-27	8-22	28-13
Mean(m)	35	28	35	14	21
Stand. dev.(S)	9.5	8.2	4.8	5.1	6.2
(s/m)×100	27	29	14	36	30

Table 6. Sample B: Results of particle size distribution (n=10).
(Results given on air dry basis.)

Fraction	Clay	Silt	Total sand	Fine sand	Med. + Coarse
Range	12-70	48-11	38-19	7-13	4-14
Mean (m)	43	30	24	10	11
Stand.dev. (S)	16	12	7	2.3	4
(s/m)×100	37	40	30	23	38

Few precautions have to be taken in conventional procedures with gypsiferous samples, especially when gypsum exceeds 5%:

- Correction of Stokes' constant according to gypsum concentration (Vieillefon, 1976)(cf. Table 7).
- Partial insolubilization of gypsum by barium chloride (Bascomb, Hesse, Vieillefon, Matar, Douleimi....).
- Inversion of sampling order to diminish gypsum dilution effect.
- Drying precaution (Vieillefon).

Table 7. Sedimentation time for clay and silt sampling at 10 cm depth according to gypsum content (in minutes and seconds).

Gypsum percentage	0	10	20	30	40	50
Temperature 20°	4'40	4'46	4'52	4'58	5'04	5'11
Temperature 25°	4'08	4'13	4'19	4'24	4'30	4'36

CALCIUM CARBONATE

All methods are based on the reaction of calcium carbonate with diluted hydrochloric acid and the subsequent measure of:

- a. Volume of carbon dioxide evolved (volumetric calcimeter);
- b. Back titration of acid (acid titrable basilety);
- c. Loss of weight to disparition of CaCO_3 (gravimetric).

Errors may arise from an improper calibration of calcimeter, or solubilization of CO_2 in acid and manometric liquid. In addition all methods have in common a low reaction rate when dolomite is present (the latter being counted for as pure calcium carbonate) and interference of MnO_2 and organic matter decomposition by acid (the last possibility being unusual in arid zones).

Alkaline earth carbonate measured from acid neutralization is more dependent on soil/acid ratio and acid concentration. This method finds its practical application for accurate determination of low calcium carbonate percentage (Miyamoto et al., 1973).

Rapid gravimetric method is claimed to yield results not varying more than 1% on triplicate analysis in the overall range of 0 to 70% calcium carbonate (Bauer et al., 1972).

Table 8. Calcium carbonate results.

Sample	A	B
n	9	7
Range	18.5 to 24.4	14.8 to 21.4
Mean m	21	18
Stand. dev.	1.7	2.2
(s/m)×100	8	12

DETERMINATION OF ORGANIC MATTER AND NITROGEN

Problems in organic matter and nitrogen determination are generally found in highly organic soils not common in arid zones.

Interference of chloride, which is oxidized by potassium dichromate (methods Walkley & Black and method Anne) is not effective for concentration up to 2400 ppm chloride (Viswanatman) and may be corrected by silver sulfate if necessary. Standard deviation at 0.72% O.C. level and n=9 is 13% only for sample A.

DETERMINATION OF SOLUBLE SALTS

Evaluation of soluble salts is commonly done by saturating extract or by systematic 1/1 or 1/2.5 extracts.

- Making a saturation paste is a simple procedure: errors are expected with fine-textured soils, especially with swelling clays and high sodium content. Though estimation of saturation point is left to personnel appreciation, the saturation percentage counts among the most reproducible procedure (r.s.d. 6%).

Table 9. Determination of saturation extract sample A (n=12).

	Mean	Range	Variability (as r.s.d.%)
Saturation (%)	64	57-70	6
Elec. Conduc. (mS cm ⁻¹)	1.7	1.3-2.3	16
Sum of ions (meq/e) (Cations + Anions)/2	19.6	17-27	13

The same cannot be said of the subsequent extraction of a soil solution. The relative standard deviation as well as the variability range of electric conductivity is greater than the saturation percentage.

Suggested reasons could be:

- Though adding the same quantity of water to reach saturation, stirring may bring into solution different quantities of salts (r.s.d. 16%).

- Time of contact between soil and solution, and temperature as well, differs from one operator to another, and from place to place.
- Extraction by suction on centrifugation may extract more or less of the saturating water (cf. Table 9).

IONIC COMPOSITION OF SATURATION EXTRACT

Table 10. Variations in ion determination of A, B and water sample.

	Ca	Mg	K	Na	Cl	SO ₄	Notes	Sample
A	14	13	10	14	12	10	Variation due to extraction	A
Mean	8.3	5.2	0.4	5.5	5.5	7.9		
(s/m)×100	26	38	23	51	35	32		
(s/m)×100	25	31	63	22	25	38	Variation due to extraction	B
B mean	29	26.5	1.0	134	96	70		
Water r.s.d.	24	27	25	14	19	38	Variation due to method	Water
Average concentration	14	16	0.7	41	56	11		

A complete review of analytical problems for each element is out of our scope, but a few remarks are worthwhile to mention:

- a. Analysis of standard water sample was done together with soils A and B. Water sample referred to has a concentration in all elements averaging results of A and B (see Table 10). Variation of water results depends on methods used to determine each element.
- b. Variation in analysis of samples A and B is greater because of the extraction process.
- c. The high value found for potassium is probably due to sodium interference.
- d. As far as classification of soils is concerned, the most apparent difficulty lies in the application of the sodium absorption ratio concept. SAR calculated from mean values of Ca, Mg and Na in saturation extract is 2.4 meq/l^{-1} . This value gives a calculated (Richard's Formula) exchangeable sodium value 2.2 meq/100 g , while the average found by analysis is 3.7 meq/100 g .

EXCHANGEABLE CATION AND CATION EXCHANGE CAPACITY

Determination of characteristics of the exchangeable complex of arid soils is actually the most troublesome analytical process. **To make things worse**, no reference procedure exists and possible correlation of cation exchange capacity either with clay and organic matter percentage or air-dry water content, or saturation percentage, are not applicable in soils containing appreciable amounts of calcium carbonate and gypsum.

Because exchangeable cations are to be removed from soil exchange sites prior to determination exchange capacity, the problems for determining CEC and exchangeable cations, sodium for instance, are similar and closely linked. **Errors are likely to accumulate and exchangeable sodium percentage will be affected by a double source of imprecision: the first due to CEC, the second due to exchangeable Na evaluation.**

Cation exchange includes absorption on exchange sites of clay, chemical reaction on functional groups of organic matter, and adsorption on the surface of crystalline particles. **Each of these phenomena is different from a physico-chemical point of view. Generally, three types of problems exist:**

- a. Those inherent to the definition of cation exchange capacity;
- b. Those inherent to the method used; and
- c. Those inherent to the technique.

Cation exchange is defined relative to a given exchanger and not absolutely. **The related error is a different CEC or a different amount of exchangeable sodium extracted according to the extracting solution.** (Ammonium acetate extracting less sodium than barium chloride for instance.)

Definition

Cation exchange is not an independent process. Permanent equilibrium between soluble and exchangeable forms of cations takes place, making it difficult to separate a specific form. This relationship has been demonstrated by Richard et al. (1954) with equation: $y = 0.0145; x = 0.0126;$ and $r = 0.923$ where y stands for exchangeable sodium ratio (exchangeable complex); x for sodium adsorption ratio (soil solution, i.e. saturation extract). **The interrelationship between soluble and exchangeable forms of cations leads to three types of errors:**

- a. An overestimation of exchangeable cations, by dissolution of calcium carbonate, calcium sulfate and/or sodium chloride.
- b. The extracting solution dissolves divalent cations, and introduces in the soil sample an artificial competition between calcium and sodium, for instance. An incomplete replacement is found where sodium is replacing cation.
- c. Substraction of soluble salts as found in saturation extracts, apart from sodium hydrolysis, adds another source of error: the variation of sodium found in saturation extract (cf. Table 9).

Method used

The second group of errors arises from the method used. Though many have been proposed, the original ammonium acetate method (Bower, 1952) is often referred to as "conventional" or "standard." The shortcomings of this method have been outlined (Okazaki et al., 1964; Polemio and Rhoades, 1977).

- a. In the saturation step (by sodium acetate pH: 8.2):
 - Calcium dissolved from carbonate and gypsum competes with sodium for occupying exchange sites and the situation is incomplete.
- b. In the washing step (by a minimum quantity of ethanol).
 - Ion competition and sodium hydrolysis occurs if washing is too energetic.
 - Incomplete removal of saturating sodium solution held by capillarity occurs if washing is too mild.
- c. In the replacement step (normal and neutral ammonium acetate solution).
 - Incomplete replacement of Na by ammonium occurs.

Technique used

The third group of difficulties, and not the least, comes from the technique used. Two systems are possible: leaching (column), or mixing--centrifuging (batch). Sources of errors are:

- Improper soil solution contact because of channeling (column).
- Loss of exchangeable material by over-dispersion during washing step (if centrifugation speed is too slow) or difficulty in re-dispersing soil (if speed is too high)(batch method).

Table 11. CEC. Results of A and B samples.

	n	Mean	s	r.s.d.	range
A	9	.19	4.6	24	11 to 26
B	8	21	10.8	51	10 to 35

EXCHANGEABLE CATIONS

Exchangeable cations may be determined in the first step of CEC in an excess of saturating solution, providing the saturating cation does not preexist as an exchangeable one.

Theoretically, saturating cations, also called index cations, should have a greater affinity for exchange sites than Ca, Mg, Na, K. The saturating solution should not, in addition, dissolve soluble salts. To fulfill these conditions it should have a very low dielectric constant, in order to leave sodium salt undissolved. In other words it should be an organic solution, the index cation being fixed by a covalent bond. It has consequently a very weak affinity for exchange sites.

- Several approaches were made by using mixtures of organic and inorganic solutions (alcoholic ammonium chloride--Tucker, 1971; triethanolamine solutions such as barium chloride--Mehlich, 1948; Bascomb, 1963), but none is free from errors.

The first method does not eliminate the need for washing out soluble sodium salts (by glycol, ethanol to avoid hydrolysis of Na). The second one is affected by a secondary reaction of barium with gypsum and calcium carbonate.

We may expect a very low level of precision and accuracy for CEC and exchangeable cations, the effect of errors being greater for Ca and Na, lower for K and Mg. We have discussed above the low precision of exchangeable sodium. Complete results are shown in Tables 12 and 13.

Table 12. Sample A: exchangeable sodium.

No.	ENa (meq/100 g) ^a	ESP ^b	Extraction	Correction
A 23	0.5	4	NH ₄ OAc	
A 9	1.08	5	NH ₄ OAc	Minus Na in sat. ext.
A 31	1.5	8	NH ₄ OAc	
A 10	1.5	8	n.i.a.	Corr. for sol.
A 3	3.1	27	NH ₄ OAc	
A 21	6.37	34	n.i.a.	
A 13	11.7	44	NH ₄ OAc	
-	3.7	18.4		mean (n=7)
Does not follow Gauss curve				stand. deviation

^aENa = is given as meq/100 g 105°C dry soil

^bESP = (ENa × 100)/C.E.C.

Table 13: Sample B: Exchangeable sodium.

Sample No.	ENa ^a	ESP	Extraction	Calculations
B 20	3.9	21	n.i.a. ^b	n.i.a.
B 30	4.0	22	NH ₄ OAc pH 7.0	n.i.a.
B 3	4.2	12	NH ₄ OAc pH 7.0	Minus Na in sat. ext.
B 11	5.9	37	n.i.a.	
B 8	7.0	63	NH ₄ OAc	Minus Na in sat. ext.
B 22	8.3	79	NH ₄ OAc	
B 12	12.2	42	NH ₄ OAc	Minus Na in sat. ext.
-	6.5	39	-	n.i.a.
Distribution does not follow a Gauss curve				mean value (n=7)

^aENa = is given as meq/100 g 105°C dry soil.

^bn.i.a. = no indications available

PHOSPHORUS

The measure of liability of soil phosphorus is affected like the measurement of CEC, by a lack of absolute definition. Liability is assessed by the quantity extracted by a given method when it correlates with plant absorption in field or pot experiment. Imprecision in the definition exists at plant level and at the extracting solution level.

Inaccuracy is due to incorrect choice of method with regard to soil properties. Imprecision is due to nonrespect of standard conditions whatever method is used, for the same extracting solution, (i.e. same reagent, same concentration, same pH...). Deviations from standard procedure may be, among others:

- Soil storage time: available phosphate may increase by 14% according to Nowosielski (cited by Batten, 1978).
- Time and speed of shaking soil with reagent.
- Time and mode of contact between soil and solution, soil solution ratio. These remarks apply for each reagent.

To mention only the methods using chemical reagents in calcareous soils:

- NaHCO_3 pH 8.5 (Olsen).
- NaOH N/10 (Saunders).
- NaHCO_3 NH_4 pH 8.5 (Olsen-Dabin).

Collaborative study on soil A gave a very close agreement on liable phosphorus (NaHCO_3 pH 8.5 for 4 det. only) while the results of total phosphorus show a greater dispersion.

Table 14. "Available" and total phosphorus, sample A.

Sample	A1	A4	A13	A14	-	n	mean
Avail. P (ppm)	11	9	10	10	-	4	10
Sample	A3	A5	A7	A10	A23	-	-
Total (ppm)	1600	2190	1830	3240	8901	5	1950
Method	HClO_4	HClO_4	HNO_3	-	4NO_3	-	-

(Note that the high values of total phosphorus are probably due to fertilizers).

DETERMINATION OF GYPSUM

Table 15. Sample B: gypsum percentage.^a

No.	Gypsum (%)	Method
B 11	5.3	n.d.a.
B 19	9.8	n.d.a.
B 5.	10.75	Difference in Acetone precipitates of 1/20 and saturation extract
B 22	11.2	Precipitation by Acetone
B 8	12.5	Dissolved in boiling (NH ₄) ₂ CO ₃ / gravimetry BaCl ₂
B 12	14.2	Acetone/Electric conductivity
B 13	14.5	n.d.a.
B 17	14.7	n.d.a.
	11.6	mean value (n=10)
	3.1	standard deviation
	27	relative standard deviation %

^aGypsum percentage is given on air-dry weight basis.

Comments

If the results are lower than true value, it may come from a too high soil/solution ratio, complete dissolution of gypsum not being achieved (cf. Table 16).

Table 16. Dissolution of gypsum: soil solution ratios in water (based on 2.6 q/l solubility, from Hesse).

Gypsum content of soils %	0-1	1-2	2-5	5-10	10-20
Soil/Solution ratio	1/5	1/10	1/20	1/50	1/100

Otherwise there is no difficulty and practically no potential source of error in gypsum determination, though results cannot be expressed on oven-dry basis.

- A rapid method, based on loss of weight by controlled heating and rehydration makes it possible to measure both gypsum concentration (with a relative standard deviation of 5%) and hygroscopic water

content (Vieillefon, 1978).

CONCLUSIONS

We can make two kinds of remarks to conclude. The first is intended to the staff of laboratories: analysts in each laboratory must evaluate, time to time, and for each method: its precision (measured as relative standard deviation of ten replicates at three different levels of the range covered by the method) and its accuracy (estimated as the deviation from the "true value" of a reference sample).

In addition to that, he must detect para-analytical sources of errors, particularly important in soil analysis (soil sample preparation, storage and subsampling).

- a. By multiple-cross checking of results using approximate relationships between soil properties, for instance:
 - Clay % versus water retention, clay % + silt % + O.C % versus CEC.
 - Ionic balance in solutions.
 - Ionic concentration and electric conductivity (allowance being made for $\frac{CA}{NA}$ and/or SO_4/Cl ratios).
 - Carbonate bicarbonate and pH.
 - Proportionality between ESP and SAR.
 - Results of analysis should be expressed with a number of digits in accordance with the variation coefficient of replicate determination on a reference sample.
- b. By using methods diminishing human coefficient of errors (for instance water saturation percentage by capillarity procedure (Longenecker) rather than hand mixing and stirring).
- c. By reducing the number of steps of each method to a reasonable minimum (for instance two steps CEC instead of three, eliminating errors due to washing step).
- d. By limiting results obtained by difference.

The second kind of remark is directed to the potential users of results. A great deal of analysis has been made through the world and its compilation might be useful at a regional level for mapping, for evaluating salinity

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