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Analytical results of the saturation extracts of the
second comparative study

C. Sonneveld

Naaldwijk [1976]
Netherlands

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Introduction

The I.S.H.S. Working Group on Standardisation of Analytical Methods held its second meeting at Naaldwijk, The Netherlands on April 14th and 15th, 1975. At this meeting it was decided to make a second comparative study. The saturation extract would be used as the reference method. Fourteen laboratories wanted to participate in the comparative study for routine soil testing and six in the comparison of saturation extract preparation. The Glasshouse Crops Research Station at Naaldwijk would send 15 samples of glasshouse soils to all participants in both studies. Results of the routine soil testing study would be sent to Dr. G. Hoffman at Karlsruhe.

Results of the saturation extract study would be collected by the Research Station at Naaldwijk. In this report the results of the saturation extract study will be discussed.

Materials, methods and instructions

In the beginning of June, 1975 fifteen soil samples had been sent to the participants. The samples were taken from glasshouse soils in the western part of The Netherlands. The soil types are listed in appendix 1.

Instruction for preparation of saturated soil pastes were provided and are given in appendix 2.

As a first step the participants were asked to saturate a portion of each soil sample, to determine the water content at saturation and to report the results.

At the end of february 1976 four laboratories had sent the results of this first preparation. Agreement between the water contents at saturation as determined by the different laboratories was acceptable. The participants were then asked to continue the study by preparing saturated soil pastes again and by carrying out the chemical analysis in the extracts. At least the following determinations would be made:

- electrical conductivity (EC)
- nitrogen (N), if possible NO_3 and NH_4 separately
- phosphate (P)
- potassium (K).

In this report EC is given as mmho.cm^{-1} at 25°C , P as mg.l^{-1} and N and K as me.l^{-1} . The water contents (M-values) are given as g water per 100 g oven-dry soil.

At Naaldwijk a determination of the total ionic composition of the saturation extracts is executed. The same is done by ADAS at Leeds.

The methods used for the chemical analysis by the participants are described in appendix 3.

One of the participants did not send the analytical results. In this report the laboratories will be denoted by the letters A till E (see appendix 4).

Results

M-values (first comparison).

For the first comparison of the M-values of the saturated paste four laboratories sent their results. The data are given in appendix 5. On average the following values have been found.

<u>Laboratory</u>	<u>M-value</u>
A	69
B	66
C	66
D	75.

Laboratory D has found the highest values and was asked to pay attention to this aspect. Furthermore the agreement was such that it was decided to prepare the saturated paste for the chemical analysis.

M-values

The M-values of the saturated paste of the second preparation are given in appendix 6. The following average values have been found.

<u>Laboratory</u>	<u>M-value</u>
A	67
B	65
C	64
D	67
E	67.

The values found by the laboratories B and C are somewhat lower than those found by the others. However, the differences are small.

E.C.

The analytical results are given in appendix 7. Laboratory D did not determine the E.C. Laboratories B and E determined the E.C. at 20°C. For comparison the E.C. at 25°C was calculated by the equation $E.C._{25} = 1.111 E.C._{20}$. Laboratory C determined the E.C. at room temperature, which was about 22°C. Correction to 25°C would increase the values about 6%. On average the following values have been found.

<u>Laboratory</u>	<u>E.C.</u>
A	5.08
B	6.23
C	4.9
E	4.88.

The laboratories C and E show a very good agreement. The average value of laboratory A is only slightly higher. The values of laboratory B are significantly higher than those of the others.

Nitrate

The results are given in appendix 8. The following average values have been computed.

<u>Laboratory</u>	<u>NO₃-contents</u>
A	24.2
B	20.7
C	23.0
D	22.3
E	26.7.

The values of laboratory E are significantly higher than those of all the others. Among the other laboratories significant differences are found only between A and B.

Ammonium

The results of the ammonium determination are presented in appendix 9. The average values are as follows.

<u>Laboratory</u>	<u>NH₄-content</u>
A	0.24
B	0.7
C	0.42
D	0.71.

The results of the laboratories B and D show on average a good agreement. Laboratory C found lower contents and laboratory A has found the lowest values.

Phosphate

The results of this determination are given in appendix 10. The following average values have been computed.

<u>Laboratory</u>	<u>P-content</u>
A	10.2
B	8.7
C	10.0
E	10.1.

The content found by laboratory B is significantly lower than those found by the others.

Potassium

The results are listed in appendix 11. On average the following values have been found.

<u>Laboratory</u>	<u>K-content</u>
A	5.1
B	5.0
C	5.5
D	4.8
E	4.6.

Generally there is a good agreement between the results. The values found by C are significantly higher than those found by B, D and E. Furthermore there is a significant difference between E and A.

Ionic composition

The laboratories A and B had determined all the principal ionic constituents. The analytical data are collected in appendix 12.

On average the following values have been computed.

<u>Determination</u>	<u>Laboratories</u>	
	<u>A</u>	<u>B</u>
K ⁺	5.1	5.0
Na ⁺	10.2	9.3
Ca ⁺⁺	32.6	33.9
Mg ⁺⁺	15.3	17.3
NH ₄ ⁺	0.2	0.7
Sum of Cations	<u>63.4</u>	<u>66.2</u>
NO ₃ ⁻	24.2	20.7
Cl ⁻	10.3	12.1
SO ₄ ⁻	26.9	28.5
HCO ₃ ⁻	1.6	8.0
H ₂ PO ₄ ⁻	0.2	0.3
HPO ₄ ⁻	0.3	
Sum of Anions	<u>63.5</u>	<u>69.6</u>

The average values of the determinations show an acceptable agreement, with the exception of bicarbonate. However, the analytical data of several determinations in itself show great differences as will be found in appendix 12. This is the more surprising as the methods of determination of both laboratories are mostly quite the similar as can be found in appendix 13.

Conclusions

This comparative study shows that saturation extracts of various soils can be prepared comparably by different laboratories. The analytical data of the determination of the electrical conductivity, nitrate, phosphate and potassium show relatively small differences between laboratories. The differences between the ammonium determination are much larger, but the quantities of ammonium which have been found are only small. A proper comparison of the total ionic composition of the saturation extract would require the participation of a larger number of laboratories in the study.

Appendix 1

Soil type of the samples collected

Sample nr.	Soil type	Organic matter % *
1	peaty loam	23
2	clay loam	9
3	loam	10
4	loam	8
5	loamy sand	10
6	sand	4
7	loam	18
8	sandy loam	8
9	peaty loam	24
10	clay loam	14
11	sand	9
12	loam	12
13	peaty loam	28
14	sand	4
15	loamy sand	6.

* loss - on - ignition at 600°C.

Appendix 2

Preparation of saturated soil pastes

Procedure of the United States Salinity Laboratory

(U.S.D.A., Agriculture Handbook no. 60, method 2)

Prepare the saturated soil paste by adding distilled water to a sample of soil while stirring with a spatula. The soil-water mixture is consolidated from time to time during the stirring process by tapping the container on the workbench. At saturation the soil paste glistens as it reflects light, flows slightly when the container is tipped, and the paste slides freely and cleanly off the spatula for all soils but those with a high clay content. After mixing, the sample should be allowed to stand for an hour or more, and then the criteria for saturation should be rechecked. Free water should not collect on the soil surface nor should the paste stiffen markedly or lose its glistening appearance on standing. If the paste does stiffen or lose its glisten, remix with more water.

Because soils puddle most readily when worked at moisture contents near field capacity, sufficient water should be added immediately to bring the sample nearly to saturation. If the paste is too wet, additional dry soil may be added.

The amount of soil required depends on the measurements to be made, i.e., on the volume of extract desired. A 250- ml sample is convenient to handle and provides sufficient extract for most purposes. Initially, the sample can be air-dry or at the field-moisture content, but the mixing process is generally easier if the soil is first air-dried and passed through a 2-mm sieve.

Commentary on the above procedure

When the size of the soil sample is about 250 ml, the diameter of the container should be 10 - 12 cm.

The easiest criterion for saturation is obtained when a diametral groove is drawn along the whole depth through the paste with the spatula. With the exception of both ends of the groove near the container wall, the groove should fill up and disappear within a few seconds.

The rechecking of the groove criterion after the period of standing should be done after stirring (the only way to alter the moisture

content of the paste, when this is necessary, is remixing, thus stirring, with more water or soil). The period of standing must be neither too long (denitrification) nor too short (incomplete dissolution of sparingly soluble salts). A period of two hours is appropriate. Free water often collects on the surface of sandy soils on standing. This should be neglected. The free water mostly disappears completely on stirring. The pastes of clayey or peaty soils often need remixing with more water after standing. Glasshouse soils mostly do not give puddling difficulties. The wetting of these soils, therefore, may be done gradually. It makes a difference whether field-moist or dried soil samples are saturated. In the former case, the saturation moisture content is higher than in the latter case. From a diagnostic point of view, field-moist samples are preferable.

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31-5-1975

Appendix 3

Methods of determination

Conductivity

- A - measured at room temperature and referred to 25°C
- B - referred to 20°C
- C - measured at room temperature (about 22°C)
- D -
- E - measured at 20°C.

Nitrate

- A - specific ion electrode
- B - titrimetrically after reduction to ammonium with Devardas alloy
- C - specific ion electrode
- D - auto analyser "Technicon"
- E - specific ion electrode.

Ammonium

- A - titrimetrically after distillation with MgO
- B - titrimetrically after distillation with MgO
- C - specific ion electrode
- D - auto analyser "Technicon"
- E -

Phosphate

- A - colorimetrically, molybdenum blue method with ascorbic acid as reducing agent
- B - colorimetrically, molybdenum blue method
- C - colorimetrically, molybdenum blue method
- D -
- E - colorimetrically, molybdenum blue method with ascorbic acid as reducing agent.

Potassium

- A - flame photometrically
- B - flame photometrically
- C - flame photometrically
- D - flame photometrically
- E - flame photometrically

Appendix 4

List of participants

- A. Glasshouse Crops Research and Experiment Station,
Naaldwijk, Netherlands
- B. Agriculture Development and Advisory Service,
Leeds, England
- C. Laboratorium voor Analytische en Agrochemie,
Gent, België
- D. Institute for Soil Fertility,
Haren, Groningen, Netherlands
- E. Glasshouse Crops Research Institute,
Littlehampton, England.

Appendix 5

M-values saturated soils.
First preparation

Sample nr.	Naaldwijk	Gent	Leeds	Groningen
1	99	89	92	106
2	80	77	68	86
3	72	73	66	80
4	51	50	48	57
5	70	70	69	73
6	42	37	38	43
7	82	77	89	92
8	57	57	53	63
9	93	86	88	103
10	79	76	73	89
11	56	51	57	62
12	67	65	64	75
13	111	114	105	118
14	40	38	42	40
15	41	37	38	44
Average	69.3	66.5	66.0	75.4

x y₁ y₂ y₃

Regression equations:

$$y_1 = 0.991 x - 2.2$$

$$y_2 = 0.931 x + 1.4$$

$$y_3 = 1.098 x - 0.7$$

Appendix 6

M-value saturated soil

Sample	A	B	C	D	E
1	94	88	92	91	94
2	74	68	71	73	75
3	68	66	65	68	69
4	48	46	51	49	52
5	67	66	69	76	66
6	41	38	34	42	40
7	79	79	76	77	80
8	55	52	54	54	56
9	95	88	83	89	91
10	76	72	73	73	77
11	57	57	48	59	50
12	65	64	65	66	67
13	106	104	105	108	111
14*	38	42	36	42	36
15	38	38	37	38	38
Average	67	65	64	67	67

x y₁ y₂ y₃ y₄

	D	E	A	B	C	Confidence level of differences (P)
D						+ 95% ≥ P < 99%
E	-					++ P ≥ 99%
A	-	-				
B	++	+	+			
C	++	++	++	-		

<u>Regression equations:</u>		<u>r</u>
y ₁ = 0.92 x + 3.0		0.993
y ₂ = 0.97 x - 0.5		0.983
y ₃ = 0.94 x + 4.5		0.987
y ₄ = 1.03 x - 1.8		0.991

Appendix 7

E.C.

Sample nr.	A 25°C	B* 25°C	C**	D***	E 25°C*
1	6.30	9.24	6.0		6.33
2	3.24	4.39	3.1		2.91
3	2.92	3.70	2.8		2.62
4	14.60	16.63	13.5		13.39
5	2.78	3.23	2.7		2.67
6	6.30	8.83	6.5		6.35
7	7.38	8.40	6.9		6.89
8	4.36	5.17	4.3		4.08
9	2.88	3.44	3.1		2.81
10	2.47	3.72	2.5		2.38
11	1.88	2.76	1.9		1.99
12	1.98	2.43	1.9		2.03
13	7.10	7.35	6.6		6.89
14	4.68	5.22	4.7		4.42
15	7.38	9.00	7.5		7.40
Average	5.08	6.23	4.9		4.88

x y₁ y₂ y₄

* E.C. given at 20°C. E.C. at 25°C calculated by the equation
 $EC_{25} = 1.111 EC_{20}$.

** Reference temperature not mentioned. Measured at room temperature (about 22°C)

*** not determined.

	B	A	C	E
B				
A	++			
C	++	-		
E	++	-	-	

		<u>r</u>
<u>Regression equations:</u>	y ₁ = 1.118 x + 0.55	0.983
	y ₂ = 0.922 x + 0.25	0.998
	y ₄ = 0.927 x + 0.17	0.997.

Appendix 8

NO₃ (me/l)

Sample nr.	A	B	C	D	E
1	21.9	16.6	21.6	21.9	21.4
2	10.7	7.8	13.4	11.8	9.6
3	10.6	5.6	10.7	10.2	10.0
4	98.2	79.0	85.4	88.2	103.6
5	9.9	4.6	10.9	10.9	14.4
6	28.1	28.6	31.7	27.1	23.4
7	37.6	27.7	34.0	36.9	40.0
8	19.4	20.2	17.0	18.0	22.9
9	8.5	9.5	8.8	8.6	12.4
10	3.5	3.5	3.1	3.5	7.4
11	3.9	4.9	3.9	3.0	8.0
12	1.3	0.8	1.3	0.4	5.7
13	39.9	36.1	35.0	36.4	44.3
14	22.2	20.0	21.6	20.9	30.4
15	47.9	45.9	46.1	37.1	46.4
Average	24.2	20.7	23.0	22.3	26.7

x y₁ y₂ y₃ y₄

	E	A	C	D	B
E					
A	+				
C	++	-			
D	++	-	-		
B	++	++	-	-	

Regression equations:

y ₁	=	0.83 x + 0.62	0.988
y ₂	=	0.87 x + 1.89	0.996
y ₃	=	0.88 x + 0.99	0.996
y ₄	=	1.01 x + 2.29	0.991.

Appendix 9

NH₄⁺ (me/l)

Sample nr.	A	B	C	D	E**
1	0.06	0.6	0.21	0.44	
2	0.04	1.0	< 0.14	0.57	
3	0.36	0.6	< 0.14	0.64	
4	1.34	3.0	1.54	2.28	
5	0.14	0.7	0.51	0.39	
6	0.28	0.7	0.63	0.61	
7	0.05	0.2	0.50	0.75	
8	0.06	0.7	0.31	0.95	
9	0.25	0.5	0.29	0.50	
10	0.04	0.2	0.17	0.75	
11	0.24	0.3	0.41	0.40	
12	0.16	0.3	< 0.14	0.80	
13	0.23	0.5	0.44	0.51	
14	0.22	0.3	0.48	0.45	
15	0.18	0.6	0.41	0.55	
Average	0.24	0.7	0.42*	0.71	

x y₁ y₂ y₃

* 0.14 counted as 0.14

** not determined.

	D	B	C	A
D				
B	-			
C	++	++		
A	++	++	-	

		r
<u>Regression equations:</u>	y ₁ = 1.90 x + 0.22	0.895
	y ₂ = 0.96 x + 0.19	0.880
	y ₃ = 1.24 x + 0.40	0.854.

Appendix 10

P (mg/l)

Sample nr.	A	B	C	D*	E
1	7.8	7.0	9.0		7.4
2	4.4	4.4	4.6		4.5
3	11.2	8.4	9.8		9.2
4	6.4	6.0	7.2		5.7
5	10.3	9.8	11.6		10.6
6	10.0	8.5	8.2		9.9
7	9.2	7.3	8.7		8.5
8	8.8	6.4	9.0		8.4
9	5.9	4.6	5.2		9.2
10	8.0	7.2	7.9		9.0
11	8.2	5.6	8.7		7.8
12	10.0	8.6	10.0		10.0
13	10.2	9.2	10.3		10.3
14	11.5	10.4	10.9		12.2
15	31.8	27.8	29.3		28.4
Average	10.2	8.7	10.0		10.1

* not determined x y₁ y₂ y₄

	A	E	C	B
A				
E	-			
C	-	-		
B	++	++	++	

		<u>r</u>
<u>Regression equations:</u>	y ₁ = 0.88 x - 0.24	0.991
	y ₂ = 0.89 x + 0.89	0.990
	y ₄ = 0.85 x + 1.41	0.981

Appendix 11

K⁺ (me/l)

Sample nr.	A	B	C	D	E
1	6.5	7.2	7.1	6.3	6.7
2	0.8	0.7	0.7	0.8	0.7
3	2.8	2.6	2.8	2.6	2.7
4	8.8	8.8	8.0	7.9	7.7
5	4.7	3.9	5.2	4.3	4.4
6	6.3	6.6	7.2	5.7	6.2
7	8.6	7.2	8.2	7.7	7.3
8	3.7	3.1	4.1	3.4	3.7
9	2.9	2.6	3.5	2.7	3.1
10	1.7	1.5	2.1	1.7	2.5
11	0.8	0.8	0.9	0.8	0.7
12	1.2	1.5	1.2	1.1	1.5
13	5.6	5.5	6.1	5.0	4.5
14	9.0	8.6	10.0	8.5	7.2
15	13.2	14.1	15.2	13.2	9.5

Average	5.1	5.0	5.5	4.8	4.6
	x	y ₁	y ₂	y ₃	y ₄

	C	A	B	D	E
C					
A	-				
B	+	-			
D	++	-	-		
E	++	+	-	-	

		<u>r</u>
<u>Regression equations:</u>	y ₁ = 1.02 x - 0.25	0.989
	y ₂ = 1.08 x - 0.02	0.989
	y ₃ = 0.96 x - 0.11	0.997
	y ₄ = 0.74 x + 0.80	0.978.

Appendix 12

Laboratory A

Ionic composition of saturation extracts

sample nr.	K	Na	Ca	Mg	NH ₄	Σ	NO ₃	Cl	SO ₄	HCO ₃	H ₂ PO ₄	HPO ₄	Σ
1	6.5	14.1	41.5	21.3	0.1	83.5	21.9	14.5	46.9	1.6	0.1	0.2	85.2
2	0.8	6.0	28.0	6.0	0.0	40.8	10.7	4.4	24.0	2.0	0.0	0.2	41.3
3	2.8	5.3	17.5	8.9	0.4	34.9	10.6	5.2	19.1	1.3	0.2	0.3	36.7
4	8.8	40.7	88.7	44.4	1.3	183.9	98.2	46.5	35.7	2.0	0.1	0.2	182.7
5	4.7	2.2	15.3	8.8	0.1	31.1	9.9	2.5	15.0	1.5	0.2	0.2	29.3
6	6.3	11.4	42.2	19.5	0.3	79.7	28.1	12.2	37.4	0.8	0.2	0.2	78.9
7	8.6	14.9	45.4	23.7	0.0	92.6	37.6	15.0	37.4	1.3	0.2	0.3	91.8
8	3.7	7.2	32.4	10.0	0.1	53.4	19.4	8.1	24.8	1.9	0.1	0.4	54.7
9	2.9	6.7	18.3	6.2	0.2	34.3	8.5	5.2	20.5	1.4	0.1	0.1	35.8
10	1.7	5.4	16.9	5.2	0.0	29.2	3.5	5.1	20.6	1.5	0.1	0.4	31.2
11	0.8	4.7	10.2	7.4	0.2	23.3	3.9	3.2	13.4	1.9	0.1	0.3	22.8
12	1.2	7.4	10.7	4.6	0.2	24.1	1.3	5.6	14.1	2.1	0.1	0.4	23.6
13	5.6	11.1	55.4	19.1	0.2	91.4	39.9	12.0	37.7	1.4	0.3	0.2	91.5
14	9.0	7.0	27.8	11.3	0.2	55.3	22.2	6.8	23.2	1.3	0.2	0.3	54.0
15	13.2	8.6	39.1	32.5	0.2	93.6	47.9	7.8	33.0	1.3	0.8	0.5	91.3

Appendix 12

Laboratory B

Ionic composition of saturation extracts

sample nr.	K	Na	Ca	Mg	NH ₄	Σ	NO ₃	Cl	SO ₄	HCO ₃	H ₂ PO ₄	HPO ₄	Σ
1	7.2	14.8	47.4	25.1	0.6	95.1	16.6	16.8	50.5	8.1	0.2	0.2	92.2
2	0.7	5.8	39.9	5.3	1.0	52.7	7.8	6.6	30.1	9.9	0.1	0.1	54.5
3	2.6	4.8	17.4	11.5	0.6	36.9	5.6	6.5	10.3	13.1	0.3	0.3	35.8
4	8.8	43.5	97.3	45.7	3.0	198.3	79.0	50.7	43.5	18.5	0.2	0.2	191.9
5	3.9	2.6	12.6	13.2	0.7	33.0	4.6	4.1	15.1	6.0	0.3	0.3	30.1
6	6.6	12.5	44.9	29.1	0.7	93.8	28.6	16.1	42.1	5.8	0.3	0.3	92.9
7	7.2	10.7	40.0	31.5	0.2	89.6	27.7	14.7	45.6	4.6	0.2	0.2	92.8
8	3.1	5.7	32.0	11.5	0.7	53.0	20.2	8.9	22.3	5.0	0.2	0.2	56.6
9	2.6	4.8	18.5	5.1	0.5	31.5	9.5	6.0	13.2	3.8	0.1	0.1	32.6
10	1.5	4.7	18.9	10.7	0.2	36.0	3.5	6.5	23.1	4.2	0.3	0.3	37.6
11	0.8	2.9	14.0	9.4	0.3	27.4	4.9	4.4	16.5	7.0	0.3	0.3	33.1
12	1.5	4.3	10.8	4.5	0.3	21.4	0.8	6.7	9.2	9.7	0.3	0.3	26.7
13	5.5	9.1	45.5	17.0	0.5	77.6	36.1	12.2	44.2	11.7	0.3	0.3	104.5
14	8.6	5.3	25.8	9.3	0.3	49.3	20.0	8.8	19.7	4.2	0.3	0.3	53.0
15	14.1	8.0	43.5	29.9	0.6	96.1	45.9	11.8	42.5	8.1	0.7	0.7	109.0

Appendix 13

Methods of determination

Sodium

- A - flame photometrically
- B - atomic absorption

Calcium and magnesium

- A - atomic absorption
- B - atomic absorption

Chloride

- A - titrimetrically with mercurinitrate
- B - titrimetrically with mercurinitrate

Sulphate

- A - turbidimetrically
- B - turbidimetrically

Bicarbonate

- A - titration till pH 5.3
- B - titration till pH 5.3 (methyl orange).