

PENNSTATE



College of Agriculture

Agronomy Series

**A COMPARISON
OF
SOIL CHARACTERIZATION
LABORATORY METHODS**

by

**Nelson C. Thurman
and
Edward J. Ciolkosz**

Agronomy Series Number 118

July 1992

**A Comparison
of
Soil Characterization Laboratory Methods**

by

Nelson C. Thurman and Edward J. Ciolkosz¹

Agronomy Series Number 118

Agronomy Department, The Pennsylvania State University

116 Agricultural Science and Industries Building

University Park, PA 16802

July 1992

¹ Soil Characterization Laboratory Director and Professor of Soil Genesis and Morphology, The Pennsylvania State University.

TABLE OF CONTENTS

		Page
Chapter 1	A Comparison of Methods of Extraction and Determination of CBD-Extractable Iron, Aluminum, and Manganese	1
Chapter 2	Comparison of Colorimetric and Atomic Absorption Methods for Analyzing KCl-Extractable Aluminum	11
Chapter 3	A Comparison of Methods of Determining BaCl ₂ -TEA Extractable Acidity	15
Chapter 4	A Comparison of the Leco Induction Furnace and Modified Walkley-Black Methods for Determining Organic Carbon	19

CHAPTER 1

A COMPARISON OF METHODS OF EXTRACTION AND DETERMINATION OF CBD-EXTRACTABLE IRON, ALUMINUM AND MANGANESE

Introduction

The Penn State University Soil Characterization Laboratory (PSUSCL) uses the citrate-bicarbonate-dithionite (CBD) method described by Mehra and Jackson (1960) to selectively extract Fe oxides and hydroxides. Although this method also extracts Mn oxides-hydroxides and non-crystalline Al oxides-hydroxides and aluminosilicates (Wada, 1989), only the Fe oxides were routinely analyzed by the PSUSCL prior to 1992.

The CBD method, which was a pretreatment for clay mineral analysis by X-ray (Ciolkosz et al., 1988), consisted of the following steps:

- (1) A bleach (NaOCl) treatment to remove the organic matter (this step, necessary in clay preparation, was used even when the soil samples were analyzed only for Fe oxides);
- (2) An extraction treatment that consisted of heating the sample in bicarbonate-citrate solution, adding dithionite, heating, centrifuging and collecting the supernatant solution and rinses (one treatment was used on most samples; only those samples which were still red or brown were subjected to additional treatments); and
- (3) A colorimetric determination of the concentration of Fe in the extract using o-phenanthroline.

Yuan and Breland (1969) noted that colorimetric methods may be subject to interferences from the extractant and that atomic absorption spectrophotometry (AAS) is generally free from such interferences. However, they did note that organic matter may interfere with the determination of Fe by AAS. Levine (1981) reported that, on the average, CBD-extractable Fe₂O₃ measured by the AAS was 0.3% less than that measured by the colorimetric method for the same samples.

Holmgren (1967) modified the Mehra and Jackson (1960) method by omitting the bicarbonate buffer. This citrate-dithionite (CD) method, modified for atomic absorption procedures, is used by the USDA-SCS National Soil Survey Laboratory (SSIS, 1991).

The objectives of this study are to:

- (1) Determine whether one extraction treatment is sufficient for the CBD-extractable Fe, Al, and Mn;
- (2) Evaluate the need to treat the soil samples with bleach (NaOCl) prior to the CBD-extraction;
- (3) Compare CBD-extractable Fe determinations by AAS and by colorimeter; and
- (4) Compare the CBD extraction method used by the PSUSCL to the CD method used by the National Soil Survey Laboratory.

Materials and Methods

For this study, 45 soil samples from the Penn State University library of characterized soils, representing a range of parent materials, drainage classes, textures, and Fe oxide contents, were selected. These soil samples were used in a study on amorphous material in Pennsylvania soils (Ciolkosz et al., 1989), and more data can be found in that publication and in the soil characterization database (Ciolkosz et al., 1992). Three laboratory standards (Ciolkosz and Dobos, 1991) were included for quality control.

Extraction methods consisted of (1) citrate-bicarbonate-dithionite (CBD) with a bleach (NaOCl) treatment (Ciolkosz et al., 1988), (2) CBD without the bleach treatment (Thurman et al., 1992), and (3) citrate-dithionite (CD) (SSIS, 1991). Aliquots of the same CBD extracts were analyzed by the o-phenanthroline colorimetric determination for Fe and by atomic absorption (AAS) for Fe, Al, and Mn (Thurman et al., 1992). The CD extracts were analyzed by AAS for Fe, Al, and Mn.

An initial subset of samples was treated to determine how many extractions were necessary to obtain complete removal of CBD-extractable Fe, Al, and Mn. The supernatant from four successive extractions on the same soil sample was collected in separate flasks and analyzed by AAS separately. In subsequent analyses, the supernatant solutions from multiple extractions on the same soil sample were combined in the same flask and analyzed as one extract.

The supernatant liquid from the bleach treatment (bleach plus a wash with NaCl solution) was collected and analyzed by AAS to determine if any Fe, Al, or Mn was lost in this step.

Two-sample T-tests were used to test for significant differences between procedures. Linear regression equations and correlation coefficients were used to test for a linear relationship between procedures. The Minitab statistical analysis package for personal computers was used for all statistical analyses (Minitab, 1991).

Results and Discussion

(1) Number of Treatments Required For Complete Extraction:

The data in Table 1.1 indicate that one extraction treatment with citrate-bicarbonate-dithionite (CBD) is not sufficient for complete recovery of extractable Fe, Al, and Mn. For most of the soil samples, all detectable levels of extractable Fe, Al, and Mn were collected in two extractions. Only the Neshaminy (09-51-01, -03, -05) and Upshur (02-23-01, -03, -07) samples still retained some brown and/or red color after the first extraction and would have required additional treatments. In most cases, levels of Fe up to 0.5 ppm were detected in extracts taken after the soil samples appeared to lose their red to brown color. Extractable Al followed a trend similar to that of Fe while Mn required two extractions for all of the samples.

Based on these results, subsequent extractions consisted of a minimum of two CBD-extraction treatments. Those soil samples which still retained some red or brown color after two treatments were subjected to additional treatments until the color completely disappeared.

Table 1.1. Content of Fe, Al, and Mn, in ppm, in successive extractions with citrate-bicarbonate-dithionite on the same soil samples.

Soil Series and Soil No. (1)	Horizon	Fe in extract, ppm			Al in extract, ppm			Mn in extract, ppm		
		Extraction Number (2)			Extraction Number (2)			Extraction Number (2)		
		1	2	3	1	2	3	1	2	3
Dormont										
02-07-02n	Ap	1.9	0.4	<0.1	23.6	6.5	<0.5	13.20	0.55	<0.05
02-07-05n	Bt2	2.7	0.5	<0.1	11.8	2.9	<0.5	2.57	0.25	<0.05
02-07-08n	Bt5	2.1	0.5	<0.1	8.3	2.5	<0.5	2.80	0.33	<0.05
Upshur										
02-23-01b	Ap	2.5	0.9	<0.1	10.5	2.2	1.8	10.30	0.11	<0.05
02-23-01n	Ap	2.1	1.1	0.2	13.1	3.3	2.9	9.80	0.25	<0.05
02-23-03b	Bt2	2.5	1.1	<0.1	11.1	2.5	1.7	0.14	<0.05	<0.05
02-23-03n	Bt2	2.1	1.4	0.2	13.6	3.0	2.8	0.15	<0.05	<0.05
02-23-07b	C1	3.2	1.5	0.2	4.1	1.3	1.2	0.86	<0.05	<0.05
02-23-07n	C1	3.8	0.8	0.2	4.0	1.4	1.2	0.92	<0.05	<0.05
Neshaminy										
09-51-01b	Ap	4.1	0.6	<0.1	31.0	6.0	<0.5	7.75	0.48	<0.05
09-51-01n	Ap	3.5	1.0	<0.1	27.5	8.5	0.6	7.45	0.42	<0.05
09-51-03b	Bt1	6.1	1.2	<0.1	30.5	6.7	0.5	7.35	0.43	<0.05
09-51-03n	Bt1	5.6	1.3	<0.1	29.0	6.6	0.5	7.25	0.42	<0.05
09-51-05n	C	3.8	1.1	<0.1	15.2	5.6	<0.5	5.55	0.22	<0.05
Cavode										
32-59-01n	Ap	1.6	0.1	<0.1	29.0	6.0	0.5	12.30	0.84	<0.05
32-59-03n	Bt1	2.2	<0.1	<0.1	21.0	3.6	<0.5	0.65	<0.05	<0.05
32-59-06n	Cg	1.1	0.1	<0.1	7.0	2.1	<0.5	1.35	<0.05	<0.05
Duffield										
36-17-01b	Ap	1.6	<0.1	<0.1	15.3	2.3	<0.5	8.30	0.25	<0.05
36-17-01n	Ap	1.5	0.2	<0.1	18.3	5.4	<0.5	8.50	0.43	<0.05
36-17-03b	Bt1	4.1	0.1	<0.1	19.5	2.2	<0.5	2.06	0.16	<0.05
36-17-03n	Bt1	3.8	0.2	<0.1	20.1	2.3	<0.5	2.00	0.15	<0.05
36-17-06b	C	3.5	0.1	<0.1	17.1	2.4	<0.5	1.56	0.05	<0.05
36-17-06n	C	3.5	0.1	<0.1	17.6	2.1	<0.5	1.46	<0.05	<0.05
Gilpin										
02-01-02b	Bt	2.2	0.1	<0.1	13.7	2.4	<0.5	1.57	0.10	<0.05
02-01-02n	Bt	2.2	0.1	<0.1	14.4	3.0	<0.5	1.55	0.12	<0.05
Hagerstown										
14-01-04b	Bt	3.3	0.1	<0.1	24.0	2.8	<0.5	3.50	0.64	<0.05
14-01-04n	Bt	3.2	0.1	<0.1	21.4	2.7	<0.5	2.88	0.24	<0.05

NOTES:

- (1) The soil number includes the County-Pedon Number-Horizon sequence used in the Penn State University Soil Characterization Laboratory (Thurman et al., 1992) along with a letter indicating that the sample was treated with bleach (b) or not treated with bleach (n) prior to the first CBD extraction.
- (2) Data for the first three extractions are presented. No detectable level of Fe, Al, or Mn was found in the final (fourth) extract.

(2) Effect of the Bleach (NaOCl) Treatment on the Extraction of Fe, Al, and Mn:

No significant differences in CBD-extractable Fe (expressed as %Fe₂O₃) and Mn (%Mn) were found between bleach-treated and untreated soil samples (Tables 1.2 and 1.3). The levels of Fe and Mn in the bleach extracts were below the detection limits for AAS. Equation (A) is the regression line for the plot of %Fe₂O₃ (no bleach) vs. %Fe₂O₃ (bleach) for all horizons.

$$(A) \quad \%Fe_2O_3 \text{ (no bleach)} = 0.220 + [0.950 \times \%Fe_2O_3 \text{ (bleach)}], R^2 = 97.9\%$$

Equation (B) shows the regression line for the plot of %Mn (no bleach) vs. %Mn (bleach) for all horizons.

$$(B) \quad \%Mn \text{ (no bleach)} = -0.00272 + [1.07 \times \%Mn \text{ (bleach)}], R^2 = 98.8\%$$

Soil samples from A horizons that were treated with bleach to remove organic matter had significantly lower levels of CBD-extractable Al (0.33% Al) than untreated samples (0.42% Al) (Table 1.3). The regression line (C) for %Al (no bleach) vs. %Al (bleach) in the A horizons has a lower correlation than that found for Fe and Mn.

$$(C) \quad \%Al \text{ (no bleach, A hor.)} = 0.181 + [0.733 \times \%Al \text{ (bleach, A hor.)}], R^2 = 60.2\%$$

Extractable Al contents in the B and C horizons are similar in both treated and untreated samples. The regression line (D) for the plot of %Al (no bleach) vs. %Al (bleach) for the B and C horizons is more in line with those for Fe and Mn.

$$(D) \quad \%Al \text{ (no bleach, B + C)} = 0.0173 + [0.995 \times \%Al \text{ (no bleach, B + C)}], R^2 = 94.6\%$$

The amount of Al recovered in the bleach extract ranged from <0.01% to 0.05% Al (average 0.02%) in the A horizon samples and from <0.01% to 0.04% (average 0.01%) in the B and C horizon samples. However, this is not sufficient to explain the difference in Al content between bleached and unbleached samples.

Probable causes for the differences in extractable Al between bleached and unbleached A horizons were not investigated in this study. The difference is only present in the A horizons, which have a higher organic matter content, suggesting that the organically-complexed Al is affected. One possible explanation is that the organically-bound Al released by the bleaching process forms an insoluble complex that is not extracted by the subsequent CBD procedure.

(3) Colorimetric vs. Atomic Absorption Methods of Measuring CBD-Extractable Fe

The %Fe₂O₃ determined by the o-phenanthroline colorimetric method averaged 0.1% to 0.2% higher than measured by AAS (Table 1.2). However, this difference was not significant for the number of samples analyzed. Yuan and Breland (1969) found that citrate in the extracting solution could interfere with AAS measurements of Fe, resulting in higher contents of Fe. That interference was not seen in this study. While the slope of the regression line (E) for the plot of %Fe₂O₃ by AAS vs. colorimeter (samples were not treated with bleach) reflects slightly higher results for the colorimetric method, the procedures are well correlated.

$$(E) \quad \%Fe_2O_3 \text{ (AAS)} = 0.0486 + [0.931 \times \%Fe_2O_3 \text{ (colorimeter)}], R^2 = 99.3\%$$

Table 1.2. Comparison of methods for extracting iron oxides (Fe₂O₃) on selected Pennsylvania soils.

Soil Series and Drainage Class	Soil No.	Horizon	Depth (cm)	% Fe ₂ O ₃				SCS- CD
				CBD Extraction		No Bleach		
				Bleach AAS	Color.	AAS	Color.	
Dormont (Moderately well drained)	02-07-02	Ap	0-18	2.4	2.5	2.7	2.7	3.0
	02-07-05	Bt2	48-58	3.6	3.8	3.8	4.1	4.0
	02-07-08	Bt5	102-132	2.7	2.9	3.1	3.3	3.3
Upshur (Well drained)	02-23-01	Ap	0-20	4.1	4.2	4.1	4.3	2.8
	02-23-03	Bt2	41-64	4.3	4.5	4.2	4.6	3.3
	02-23-07	C1	117-142	5.8	6.3	5.7	6.3	4.4
Bath (Well drained)	08-11-01	Ap	0-18	1.4	1.4	1.5	1.5	1.5
	08-11-03	Bw2	28-36	1.5	1.4	1.4	1.5	1.6
	08-11-06	Bx3	69-107	1.9	1.5	1.7	1.7	1.6
Chippewa (Poorly drained)	08-16-01	Ap	0-15	2.1	2.1	2.3	2.4	2.6
	08-16-03	Bwg	30-43	2.6	2.6	2.7	2.7	2.8
	08-16-06	Bxg3	94-130	1.3	1.4	1.4	1.4	1.8
Duncannon (Well drained)	09-05-01	Ap	0-25	1.4	1.5	1.5	1.5	1.4
	09-05-03	Bt1	43-61	2.9	3.1	3.0	3.1	2.8
	09-05-05	BC	86-102	2.4	2.5	2.4	2.5	2.0
Towhee (Poorly drained)	09-13-01	Ap	0-18	1.9	2.0	2.1	2.3	2.0
	09-13-04	Btg2	53-71	4.5	4.8	4.4	4.6	4.4
	09-13-06	Bxg2	104-127	5.2	5.6	5.1	5.6	7.4
Neshaminy (Well drained)	09-51-01	Ap	0-18	5.6	6.0	5.4	5.6	6.0
	09-51-03	Bt2	33-58	8.7	8.7	8.2	8.3	8.7
	09-51-05	C	91-163	5.4	5.7	5.8	6.3	5.8
Laidig (Well drained)	14-31-03	A	0-8	1.5	1.4	1.7	1.8	2.0
	14-31-06	Bt2	51-58	2.9	2.9	2.7	2.9	3.0
	14-31-10	Bx1	102-150	3.0	3.0	3.1	3.2	3.2
Cookport (Moderately well drained)	17-15-02	BA	5-15	3.3	3.3	3.3	3.5	3.0
	17-15-04	Bt2	25-38	2.7	2.7	2.9	3.0	2.2
	17-15-07	Bx3	84-119	2.9	2.9	2.9	3.0	2.9
Wharton (Moderately well drained)	32-53-01	Ap	0-25	2.3	2.4	2.4	2.5	2.0
	32-53-04	Btg2	48-61	3.1	3.1	3.5	3.6	2.6
	32-53-06	C	91-137	2.9	3.0	3.0	3.1	2.3
Cavode (Somewhat poorly drained)	32-59-01	Ap	0-28	2.0	2.1	2.0	2.1	1.2
	32-59-03	Bt1	41-53	2.5	2.7	2.6	2.9	2.2
	32-59-06	Cg	119-145	1.4	1.5	1.4	1.5	0.8
Duffield (Well drained)	36-17-01	Ap	0-18	1.9	2.0	2.0	2.3	1.4
	36-17-03	Bt1	30-56	5.0	5.4	4.8	5.4	4.0
	36-17-06	C	102-132	4.3	4.6	4.3	4.6	3.6
Manor (Well drained)	36-28-01	Ap1	0-13	2.7	2.9	2.9	3.1	2.7
	36-28-03	Bw	25-51	2.7	2.9	2.7	2.9	1.5
	36-28-06	C1	84-94	1.7	1.7	1.7	1.8	1.4

Table 1.2 (cont.). Comparison of methods for extracting iron oxides (Fe₂O₃) on selected Pennsylvania soils.

Soil Series and Drainage Class	Soil No.	Horizon	Depth (cm)	% Fe ₂ O ₃				SCS- CD AAS
				CBD Extraction		-- No Bleach --		
				-- Bleach -- AAS	Color.	AAS	Color.	
Lackawanna (Well drained)	45-80-01	Ap	0-18	1.5	1.5	1.8	1.8	1.8
	45-80-03	Bw2	36-51	1.2	1.2	1.3	1.3	1.1
	45-80-05	Bx1	71-135	1.3	1.2	1.2	1.2	0.6
Watson (Moderately well drained)	55-02-01	Ap	0-23	2.4	2.6	2.5	2.6	1.8
	55-02-03	Bt2	46-69	3.3	3.5	4.3	4.5	2.2
	55-02-05	Bx2	89-114	2.1	2.3	2.4	2.5	2.0
Gilpin (Standard) (Well drained)	02-01-01	Ap	0-25	1.9	1.9	1.9	1.9	2.1
	02-01-02	Bt	25-46	2.7	3.1	2.7	3.1	2.8
Hagerstown (Standard) (Well drained)	14-01-04	Bt	61-86	3.6	3.8	3.6	3.8	4.4
	14-01-04	Bt	61-86	3.5	3.6	3.7	3.8	-
	14-01-04	Bt	61-86	4.0	4.5	3.9	4.3	-
All Horizons:	Mean			2.9	3.0	3.0	3.2	2.8
	Std. Dev.			1.5	1.6	1.4	1.5	1.6
A Horizons Only:	Mean			2.4	2.5	2.5	2.6	2.3
	Std. Dev.			1.1	1.2	1.0	1.1	1.1
B & C Horizons:	Mean			3.2	3.3	3.2	3.4	3.0
	Std. Dev.			1.6	1.7	1.6	1.7	1.8

Notes:

CBD Extraction -- Citrate-bicarbonate-dithionite extraction procedure based on Mehra and Jackson (1960) and used by the Penn State Soil Characterization Laboratory (Thurman et al., 1992).

SCS-CD -- Citrate-dithionite extraction procedure based on Holmgren (1967) and used by the USDA-SCS National Soil Survey Laboratory (SSIS, 1991).

Bleach -- Samples were treated with bleach (NaOCl) prior to the CBD extraction.

No Bleach -- Samples were not treated with bleach (NaOCl) prior to the CBD extraction.

AAS -- Iron was analyzed using a Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer.

Color. -- Iron was analyzed using a Bausch & Lomb Spectronic 20 colorimeter.

Two-Sample T-Tests, 95% Confidence Interval

Comparison	Horizons	T	P	Significance
Fe, Bleach vs. No Bleach, AAS	All	-0.25	0.80	No
Fe, Bleach vs. No Bleach, Colorimeter	All	-0.40	0.69	No
Fe, Colorimeter vs. AAS, Bleach Treat.	All	-0.38	0.71	No
Fe, Colorimeter vs. AAS, No Bleach	All	-0.56	0.57	No
Fe, CBD extract. vs. SCS C-D extract.	All	0.68	0.50	No

T = T-test statistic; P = probability that the sample groups are not significantly different at the 0.05 level

Significance: No = sample groups are not significantly different; Yes = sample groups are significantly different

Table 1.3. Comparison of methods for extracting manganese and aluminum oxides on selected Pennsylvania soils.

Soil Series and Drainage Class	Soil No.	Horizon	Depth (cm)	% Mn			% Al		
				CBD Extraction		SCS- CD	CBD Extraction		SCS- CD
				Bleach	No Bleach		Bleach	No Bleach	
Dormont (Moderately well drained)	02-07-02	Ap	0-18	0.22	0.23	0.25	0.32	0.50	0.23
	02-07-05	Bt2	48-58	0.04	0.05	0.04	0.24	0.24	0.21
	02-07-08	Bt5	102-132	0.04	0.05	0.05	0.17	0.18	0.16
Upshur (Well drained)	02-23-01	Ap	0-20	0.17	0.17	0.11	0.26	0.31	0.12
	02-23-03	Bt2	41-64	0.00	0.00	0.00	0.26	0.32	0.16
	02-23-07	C1	117-142	0.01	0.02	0.01	0.11	0.11	0.08
Bath (Well drained)	08-11-01	Ap	0-18	0.04	0.04	0.04	0.26	0.41	0.25
	08-11-03	Bw2	28-36	0.02	0.02	0.02	0.24	0.27	0.25
	08-11-06	Bx3	69-107	0.04	0.04	0.04	0.15	0.15	0.14
Chippewa (Poorly drained)	08-16-01	Ap	0-15	0.10	0.10	0.11	0.26	0.42	0.23
	08-16-03	Bwg	30-43	0.06	0.06	0.07	0.24	0.26	0.25
	08-16-06	Bxg3	94-130	0.05	0.06	0.06	0.09	0.09	0.13
Duncannon (Well drained)	09-05-01	Ap	0-25	0.08	0.08	0.08	0.26	0.35	0.27
	09-05-03	Bt1	43-61	0.02	0.02	0.02	0.26	0.26	0.24
	09-05-05	BC	86-102	0.03	0.03	0.02	0.16	0.16	0.11
Towhee (Poorly drained)	09-13-01	Ap	0-18	0.03	0.05	0.04	0.20	0.30	0.18
	09-13-04	Btg2	53-71	0.07	0.07	0.05	0.30	0.30	0.36
	09-13-06	Bxg2	104-127	0.10	0.09	0.11	0.39	0.41	0.67
Neshaminy (Well drained)	09-51-01	Ap	0-18	0.14	0.13	0.13	0.62	0.61	0.61
	09-51-03	Bt2	33-58	0.13	0.13	0.13	0.63	0.60	0.69
	09-51-05	C	91-163	0.09	0.10	0.09	0.31	0.35	0.42
Laidig (Well drained)	14-31-03	A	0-8	0.42	0.48	0.45	0.31	0.50	0.35
	14-31-06	Bt2	51-58	0.01	0.01	0.02	0.28	0.29	0.28
	14-31-10	Bx1	102-150	0.08	0.08	0.07	0.26	0.28	0.28
Cookport (Moderately well drained)	17-15-02	BA	5-15	0.01	0.01	0.01	0.42	0.46	0.37
	17-15-04	Bt2	25-38	0.01	0.01	0.01	0.38	0.40	0.26
	17-15-07	Bx3	84-119	0.07	0.06	0.06	0.18	0.18	0.18
Wharton (Moderately well drained)	32-53-01	Ap	0-25	0.21	0.21	0.09	0.43	0.45	0.18
	32-53-04	Btg2	48-61	0.03	0.03	0.02	0.32	0.34	0.21
	32-53-06	C	91-137	0.05	0.05	0.03	0.25	0.25	0.13
Cavode (Somewhat poorly drained)	32-59-01	Ap	0-28	0.23	0.22	0.13	0.42	0.59	0.20
	32-59-03	Bt1	41-53	0.01	0.01	0.01	0.38	0.41	0.29
	32-59-06	Cg	119-145	0.02	0.02	0.02	0.13	0.15	0.10
Duffield (Well drained)	36-17-01	Ap	0-18	0.14	0.15	0.08	0.29	0.40	0.16
	36-17-03	Bt1	30-56	0.04	0.04	0.03	0.36	0.37	0.32
	36-17-06	C	102-132	0.03	0.02	0.02	0.32	0.33	0.29
Manor (Well drained)	36-28-01	Ap1	0-13	0.06	0.07	0.06	0.36	0.39	0.28
	36-28-03	Bw	25-51	0.04	0.03	0.02	0.28	0.30	0.13
	36-28-06	C1	84-94	0.08	0.09	0.07	0.14	0.16	0.11

Table 1.3 (cont.). Comparison of methods for extracting manganese and aluminum oxides on selected Pennsylvania soils.

Soil Series and Drainage Class	Soil No.	Horizon	Depth (cm)	% Mn			% Al		
				CBD Extraction No Bleach	% Mn Bleach	SCS- CD	CBD Extraction No Bleach	% Al Bleach	SCS- CD
Lackawanna (Well drained)	45-80-01	Ap	0-18	0.01	0.01	0.01	0.28	0.44	0.26
	45-80-03	Bw2	36-51	0.02	0.02	0.02	0.15	0.15	0.10
	45-80-05	Bx1	71-135	0.04	0.04	0.02	0.09	0.09	0.02
Watson (Moderately well drained)	55-02-01	Ap	0-23	0.03	0.03	0.02	0.27	0.30	0.17
	55-02-03	Bt2	46-69	0.00	0.00	0.00	0.32	0.44	0.15
	55-02-05	Bx2	89-114	0.00	0.00	0.00	0.19	0.25	0.19
Gilpin (Standard) (Well drained)	02-01-01	Ap	0-25	0.12	0.12	0.12	0.27	0.30	0.27
	02-01-02	Bt	25-46	0.03	0.03	0.03	0.27	0.29	0.24
Hagerstown (Standard) (Well drained)	14-01-04	Bt	61-86	0.05	0.04	0.08	0.36	0.35	0.38
	14-01-04	Bt	61-86	0.04	0.04	-	0.35	0.35	-
	14-01-04	Bt	61-86	0.07	0.05	-	0.45	0.40	-
All Horizons:	Mean			0.07	0.07	0.07	0.28	0.32	0.24
	Std. Dev.			0.08	0.08	0.08	0.09	0.09	0.02
A Horizons Only:	Mean			0.13	0.13	0.11	0.33	0.42	0.26
	Std. Dev.			0.11	0.12	0.11	0.10	0.10	0.12
B & C Horizons:	Mean			0.04	0.04	0.04	0.26	0.27	0.24
	Std. Dev.			0.03	0.03	0.03	0.11	0.11	0.15

Notes:

CBD Extraction -- Citrate-bicarbonate-dithionite extraction procedure based on Mehra and Jackson (1960) and used by the Penn State Soil Characterization Laboratory (Thurman et al., 1992).

SCS-CD -- Citrate-dithionite extraction procedure based on Holmgren (1967) and used by the USDA-SCS National Soil Survey Laboratory (SSIS, 1991).

Bleach -- Samples were treated with bleach (NaOCl) prior to the CBD extraction.

No Bleach -- Samples were not treated with bleach (NaOCl) prior to the CBD extraction.

Mn and Al in all extracts were analyzed using a Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer.

Two-Sample T-Tests, 95% Confidence Interval

Comparison	Horizons	T	P	Significance
Mn, Bleach vs. No Bleach	All	-0.13	0.90	No
Mn, CBD extract. vs. SCS C-D extract.	All	0.58	0.56	No
Al, Bleach vs. No Bleach	All	-1.69	0.09	No
Al, Bleach vs. No Bleach	A	-2.64	0.013	Yes
Al, Bleach vs. No Bleach	B & C	-0.56	0.58	No
Al, CBD extract. vs. SCS C-D extract.	All	2.92	0.004	Yes
Al, CBD extract. vs. SCS C-D extract.	B & C	1.14	0.26	No

T = T-test statistic; P = probability that the sample groups are not significantly different at the 0.05 level

Significance: No = sample groups are not significantly different; Yes = sample groups are significantly different

(4) CBD-Extraction vs. CD-Extraction Procedures For Fe, Al, and Mn

The CBD extraction tended to result in higher Fe_2O_3 contents than the CD extraction used by the National Soil Survey Laboratory, although the difference was not statistically significant (Table 1.2). No differences between the procedures were found for Mn, while the CBD extraction did produce significantly higher concentrations of Al than the CD extraction (Table 1.3). Equations F, G, and H are linear regression equations for the plots of CBD-extractable vs. CD-extractable Fe_2O_3 , Mn, and Al, respectively.

$$(F) \quad \% \text{Fe}_2\text{O}_3 \text{ (CBD, No Bleach)} = 0.745 + [0.809 \times \% \text{Fe}_2\text{O}_3 \text{ (CD)}], R^2 = 82.7\%$$

$$(G) \quad \% \text{Mn}_{\text{CBD, No Bleach}} = 0.00571 + [1.06 \times \% \text{Mn}_{\text{CD}}], R^2 = 90.2\%$$

$$(H) \quad \% \text{Al}_{\text{CBD, No Bleach}} = 0.174 + [0.613 \times \% \text{Al}_{\text{CD}}], R^2 = 42.9\%$$

Summary and Recommendations

Based on the results of this study, the following modifications in the PSUSCL procedure for CBD-extractable Fe, Al, and Mn are recommended:

- (1) Eliminate the bleach treatment, unless the soil samples are also being prepared for X-ray analysis. CBD-extractable Fe_2O_3 and Mn are not significantly affected by the elimination of the bleach step. The bleach treatment results in lower concentrations of extractable Al, possibly due to precipitation of organically-complexed Al.
- (2) Use a minimum of two extractions to ensure that all of the extractable Fe, Al, and Mn are collected. For those samples that still retain some red or brown color, repeat the extraction until the color completely disappears.
- (3) Replace the colorimetric method of determining Fe with atomic absorption spectroscopy (AAS). No significant difference was noted between the two methods of determining the Fe concentration in the extracts.

The CBD-extractable Fe data in the Penn State University Database System has primarily been analyzed using the colorimetric procedure (before 1966, Fe was analyzed by titration). The recommended modifications do not result in data that is significantly different from that generated by the old method of a bleach treatment and colorimetric determination (Table 1.2). Equation I is the regression line for the plot of CBD-extractable Fe_2O_3 as determined by the old and the modified methods.

$$(I) \quad \% \text{Fe}_2\text{O}_3 \text{ (modified)} = 0.278 + [0.895 \times \% \text{Fe}_2\text{O}_3 \text{ (old)}], R^2 = 97.8\%$$

The CBD-extraction procedure and the citrate-dithionite (CD) extraction used by the National Soil Survey Laboratory produce similar results for extractable Fe_2O_3 and Mn and for Al in B and C horizons. The correlations between the procedures for Fe_2O_3 and Mn are given in Equations F and G, respectively. The correlation for Al is not very strong.

References

- Ciolkosz, E. J., R. C. Cronce, and R. R. Dobos. 1988. Pennsylvania State University soil characterization laboratory manual. Penn State Univ. Agron. Series No. 101.
- Ciolkosz, E. J., R. C. Cronce, and R. R. Dobos. 1989. Amorphous material in Pennsylvania soils. Penn State Univ. Agron. Series No. 105.
- Ciolkosz, E. J., and R. R. Dobos. 1991. Pennsylvania State University soil characterization laboratory data summary for standard samples. Penn State Univ. Agron. Series no. 112.
- Ciolkosz, E. J., N. C. Thurman, and R. R. Dobos. 1992. Penn State University soil characterization database system. Penn State Univ. Agron. Dept.
- Holmgren, G. S. S. 1967. A rapid citrate-dithionite extractable iron procedure. Soil Sci. Soc. Amer. Proc. 31:210-211.
- Levine, E. R. 1981. Time as a factor in the genesis of soils formed from glacial till in northeastern Pennsylvania. M. S. Thesis. The Pennsylvania State Univ., University Park, PA.
- Mehra, O. P., and M. L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Seventh Natl. Conf. on Clays and Clay Minerals. pp. 317-327.
- Minitab Inc. 1991. Minitab statistical software, release 8. PC version. Minitab Inc. State College, PA.
- Soil Survey Investigations Staff (SSIS). 1991. Soil survey laboratory methods manual. Soil Surv. Invest. Rpt. No. 42. Ver. 1.0. USDA-SCS National Soil Survey Laboratory, Lincoln, NE.
- Thurman, N. C., E. J. Ciolkosz, and R. R. Dobos. 1992. Pennsylvania State University soil characterization laboratory methods manual. Penn State Univ. Agron. Series No. 117.
- Wada, K. 1989. Allophane and imogolite. p. 1051-1087 in J. B. Dixon and S. B. Weed (ed.). Minerals in soil environments. 2nd ed. SSSA Book Series, no. 1. Soil Sci. Soc. Amer., Madison, WI.
- Yuan, T. L., and H. L. Breland. 1969. Evaluation of atomic absorption methods for determinations of aluminum, iron, and silicon in clay and soil extracts. Soil Sci. Soc. Proc. 33:868-872.

CHAPTER 2

COMPARISON OF COLORIMETRIC AND ATOMIC ABSORPTION METHODS FOR ANALYZING KCl-EXTRACTABLE ALUMINUM

Introduction

Extractable, or exchangeable, aluminum (Al) ions are displaced by an unbuffered neutral salt solution (1 N KCl). Prior to 1992, the displaced Al was analyzed using a colorimetric procedure (Ciolkosz et al., 1988). In this procedure, the extracted Al is first converted to an ionic state with acid and heat to eliminate interferences due to P and Si. The color is then developed with the reagent aluminon and transmittance is analyzed with a spectrometer. Transmittance readings for standard solutions are plotted on semilog graph paper and sample concentrations are determined from the standard curve.

Yuan and Breland (1969) and Barnhisel and Bertsch (1982) note that atomic absorption spectrometry (AAS) can be used in place of colorimetric methods for determining Al extracted by neutral salts, dithionite, and oxalate solutions. Thus AAS, with a nitrous oxide-acetylene flame, can provide a suitable rapid analysis of Al in solutions. Although this is the case, Barnhisel and Bertsch (1982) recommend that methods other than AAS be used when the Al concentration is less than 2 ppm.

The objective of this study is to determine whether AAS can be used in place of the colorimetric method for determining KCl-extractable Al without resulting in significant differences in data.

Materials and Methods

The soil samples used in the study came from the following sources:

- (1) A Laidig (13 horizons) and a Buchanan (15 horizons) soil used in a study on colluvial parent material in the Ridge and Valley Province. Profile descriptions and additional characterization data can be found in the thesis by Hoover (1983) and in the soil characterization database (Ciolkosz et al., 1992).
- (2) Selected horizons (18 total) from six soils used in a study on amorphous material in Pennsylvania soils (Ciolkosz et al., 1989).
- (3) Two samples of a laboratory standard (Ciolkosz and Dobos, 1991) used for quality control.

A solution of 1 N KCl displaced extractable Al in the soil samples. The extract was collected and adjusted to a known volume as described by Thurman et al. (1992). Aliquots of the same extract were analyzed by the colorimetric method (Appendix E in Thurman et al., 1992) and by atomic absorption spectrometry (Chapter 13 and Appendix C in Thurman et al., 1992).

A two-sample T-test was used to test for significant differences between the methods of analyzing Al. A linear regression equation and correlation coefficient checked for a linear relationship between the procedures. The Minitab statistical analysis package for personal computers was used for all statistical analyses (Minitab, 1991).

Results and Discussion

No significant difference is found between the colorimetric and atomic absorption methods of determining KCl-extractable Al (Table 2.1). The linear regression analysis indicates that the two methods are highly correlated with a 1:1 relationship.

A 25X dilution factor resulting from the heat and acid treatment used in the colorimetric method is eliminated. The heat-acid treatment is used to eliminate the interference of P and Si in the Al determinations. These interferences are not apparent in the AAS procedure. The 25X dilution factor no longer appears in the soil characterization database computer program calculations for KCl-Al and must be entered manually to use the program with the colorimetric method.

Table 2.1. A Comparison of Colorimetric vs. Atomic Absorption Methods of Analyzing KCl-Extractable Al From Selected Pennsylvania Soils.

Soil Series	Soil Number	Horizon	Depth (cm)	-- KCl-Extractable Al ¹ --	
				Colorimeter ----- meq Al/ 100 g -----	AAS
Laidig	14-63-01	A	0 - 3	6.5	6.7
	14-63-02	E	3 - 36	3.3	3.6
	14-63-03	EB	36 - 46	3.1	3.3
	14-63-04	Bt1	46 - 61	4.2	4.2
	14-63-05	Bt2	61 - 79	3.8	4.1
	14-63-06	Bxt1	79 - 107	3.3	3.5
	14-63-07	Bxt2	107 - 150	3.1	3.3
	14-63-08	Bxt3	150 - 173	3.1	3.4
	14-63-09	Bxt4	173 - 201	3.0	3.1
	14-63-10	Bxt5	201 - 216	1.7	1.7
	14-63-11	2Bxt6	216 - 239	2.0	2.0
	14-63-12	2Bt1b	239 - 290	2.2	2.0
	14-63-13	2Bt2b	290 - 366	2.7	2.1
Buchanan	31-36-02	A	0 - 5	3.4	3.2
	31-36-03	E	5 - 13	3.0	2.8
	31-36-04	BEt	13 - 23	4.2	3.8
	31-36-05	Bt	23 - 43	4.4	4.3
	31-36-06	Btg1	43 - 66	5.6	5.3
	31-36-07	Btg2	66 - 84	5.5	5.1
	31-36-08	2Bxt	84 - 145	0.9	0.9
	31-36-09	3Bxtb1	145 - 168	0.1	0.1
	31-36-10	3Bxtb2	168 - 185	0.1	0.1
	31-36-11	3Bxtb3	185 - 234	0.1	0.1
	31-36-12	3Bxtb4	234 - 290	0.1	0.1
	31-36-13	3Bxtb5	290 - 330	0.6	0.5
	31-36-14	4BCtb	330 - 363	0.7	0.6
	31-36-15	4Cb	363 - 391	0.3	0.2
	31-36-16	4Crb	391 - 406	0.5	0.5

Table 2.1 (cont.). A Comparison of Colorimetric vs. Atomic Absorption Methods of Analyzing KCl-Extractable Al From Selected Pennsylvania Soils.

Soil Series	Soil Number	Horizon	Depth (cm)	-- KCl-Extractable Al ¹ --	
				Colorimeter ----- meq Al/ 100 g -----	AAS
Dormont	02-07-02	Ap	0 - 18	1.9	1.9
	02-07-05	Bt2	48 - 58	1.4	1.3
	02-07-08	Bt5	102 - 132	1.7	1.8
Upshur	02-23-01	Ap	0 - 20	1.4	1.3
	02-23-03	Bt2	41 - 64	10.1	11.2
	02-23-07	C1	117 - 142	0.0	0.0
Bath	08-11-01	Ap	0 - 18	0.9	0.8
	08-11-03	Bw2	28 - 36	2.2	2.1
	08-11-06	Bx3	69 - 107	1.3	1.2
Cookport	17-15-02	BA	5 - 15	8.3	7.8
	17-15-04	Bt2	25 - 38	5.5	5.0
	17-17-07	Bx3	84 - 119	1.3	1.4
Cavode	32-59-01	Ap	0 - 28	0.6	0.5
	32-59-03	Bt1	41 - 53	6.3	6.2
	32-59-06	Cg	119 - 145	4.2	4.6
Lackawanna	45-80-01	Ap	0 - 18	1.0	1.0
	45-80-03	Bw2	36 - 51	0.6	0.3
	45-80-05	Bx1	71 - 135	0.5	0.3
Hagerstown	14-01-04	Bt	61 - 86	3.0	3.0
	14-01-04	Bt	61 - 86	3.0	2.9
Mean				2.6	2.6
Standard Dev.				2.2	2.3
Standard Error of the Mean				0.32	0.33

NOTES:

¹ - Al extracted with 1 N KCl is analyzed by (1) a colorimetric method using the reagent aluminon or (2) atomic absorption spectrometry.

A two sample T-Test found no significant difference (95% confidence interval) between KCl-Al determined by a colorimeter (KCl-Al_{col}) and KCl-Al determined by atomic absorption (KCl-Al_{aas}).

Linear regression equation for the line that best fits the plot of KCl-Al_{aas} vs. KCl-Al_{col}:

$$\text{KCl-Al}_{\text{aas}} = -0.0892 + (1.02 \times \text{KCl-Al}_{\text{col}}), R^2 = 0.987$$

Recommendations

The colorimetric method can be replaced with the more rapid atomic absorption method for determining the Al content in KCl extracts with no significant differences in the data collected. Direct comparisons can be made between existing data analyzed by colorimetry and new data analyzed by atomic absorption.

The recommended change has been incorporated into the recently-revised Penn State University Soil Characterization Laboratory methods manual (Thurman et al., 1992).

References

- Barnhisel, R., and P. M. Bertsch. 1982. Aluminum. p. 275-300 in A. L. Page, R. H. Miller, and D. R. Keeney (Ed.). Methods of soil analysis. Part 2. Chemical and microbiological properties. Agron. No. 9 (2nd edition). Soil Sci. Soc. of Amer. Madison, WI.
- Ciolkosz, E. J., R. C. Cronce, and R. R. Dobos. 1988. Pennsylvania State University soil characterization laboratory manual. Penn State Univ. Agron. Series No. 101.
- Ciolkosz, E. J., R. C. Cronce, and R. R. Dobos. 1989. Amorphous material in Pennsylvania soils. Penn State Univ. Agron. Series No. 105.
- Ciolkosz, E. J., and R. R. Dobos. 1991. Pennsylvania State University soil characterization laboratory data summary for standard samples. Penn State Univ. Agron. Series no. 112.
- Ciolkosz, E. J., N. C. Thurman, and R. R. Dobos. 1992. Penn State University soil characterization database system. Penn State Univ. Agron. Dept.
- Hoover, M. T. 1983. Soil development in colluvium in footslope position in the Ridge and Valley Physiographic Province in Pennsylvania. Ph. D. Thesis, Penn. State Univ., Univ. Park, PA. 271 pp.
- Minitab Inc. 1991. Minitab statistical software, release 8. PC version. Minitab Inc. State College, PA.
- Thurman, N. C., E. J. Ciolkosz, and R. R. Dobos. 1992. Pennsylvania State University soil characterization laboratory methods manual. Penn State Univ. Agron. Series No. 117.
- Yuan, T. L., and H. L. Breland. 1969. Evaluation of atomic absorption methods for determinations of aluminum, iron, and silicon in clay and soil extracts. Soil Sci. Soc. Proc. 33:868-872.

CHAPTER 3

A COMPARISON OF METHODS OF DETERMINING BaCl₂-TEA EXTRACTABLE ACIDITY

Introduction

Extractable, or exchangeable, acidity is a relatively arbitrary quantity that consists of (1) exchangeable H ions, (2) H ions released from the hydrolysis of exchangeable trivalent and partially hydrolyzed Al and nonexchangeable Al, and (3) weakly-dissociated acidic groups, predominantly organic (Thomas, 1982). Over the years, numerous methods have been proposed to determine exchangeable acidity at different pH levels (see Thomas, 1982, for a review). The prevailing opinion today is to determine soil acidity at a pH near 8.3, which is the maximum pH obtainable with CaCO₃ (Thomas, 1982).

The Penn State University Soil Characterization Laboratory (PSUSCL) uses the procedure described by Peech (1965), modified for the mechanical vacuum extractor to determine acidity (Thurman et al., 1992). The National Soil Survey Laboratory (NSSL) uses the procedure described by Thomas (1982), modified for the mechanical vacuum extractor (SSIS, 1991). The PSUSCL method soaks the soil samples overnight in a 0.5 N BaCl₂ - 0.055 N TEA extracting solution buffered at pH 8.0. In the NSSL method, soil samples soak for one hour in a 0.5 N BaCl₂ - 0.2 N TEA extracting solution buffered at pH 8.2. During the vacuum extraction and replacement process, the same buffered extraction solution is used in the PSUSCL method while unbuffered 0.5 N BaCl₂ is used in the NSSL method. In both methods, the extracted acidity is neutralized with TEA and unneutralized TEA is collected for back-titration.

The BaCl₂-TEA, pH 8.2 method is considered a standard reference method for extractable acidity (SSIS, 1991). This study compares the method of determining extractable acidity used by the PSUSCL to the BaCl₂-TEA, pH 8.2 method used by the NSSL. The objective is to determine if the procedures are similar or, if data produced from the two methods are dissimilar, if modifications are warranted in the PSUSCL method.

Materials and Methods

The soil samples used in the study came from the following sources:

- (1) A Laidig (13 horizons) and a Buchanan (15 horizons) soil used in a study on colluvial parent material in the Ridge and Valley Province. Profile descriptions and additional characterization data can be found in the thesis by Hoover (1983) and in the soil characterization database (Ciolkosz et al., 1992).
- (2) Selected horizons (18 total) from six soils used in a study on amorphous material in Pennsylvania soils (Ciolkosz et al., 1989).
- (3) Two samples of a laboratory standard (Ciolkosz and Dobos, 1991) used for quality control.

BaCl₂-TEA extractable acidity for the soil samples was determined by both the PSUSCL (Thurman et al., 1992) and the NSSL (SSIS, 1991) methods.

A two-sample T-test was used to test for significant differences between the methods of analyzing Al. A linear regression equation and correlation coefficient checked for a linear relationship between the procedures. The Minitab statistical analysis package for personal computers was used for all statistical analyses (Minitab, 1991).

Results and Discussion

In 30 of the 48 soil samples analyzed, the BaCl₂-TEA, pH 8.0 method measured higher levels of extractable acidity (ranging from 0.1 to 4.1 meq/100 g higher, with an average of 1.3 meq/100 g) than the BaCl₂-TEA, pH 8.2 method (Table 3.1). This difference may be due to the longer contact time between the soil sample and the extracting solution (overnight vs. 1 hour). However, overall the trend is inconsistent and no significant difference is found between the two methods. The linear regression analysis does indicate a significant correlation between the two methods.

Table 3.1. Comparison of Methods of Determining BaCl₂-TEA Extractable Acidity on Selected Pennsylvania Soils.

Soil Series	Soil Number	Horizon	Depth (cm)	-- Extractable Acidity ¹ --	
				pH 8.0 EA ----- meq / 100 g -----	pH 8.2 EA
Laidig	14-63-01	A	0 - 3	30.7	26.6
	14-63-02	E	3 - 36	12.1	11.8
	14-63-03	EB	36 - 46	9.8	9.7
	14-63-04	Bt1	46 - 61	11.6	17.5
	14-63-05	Bt2	61 - 79	11.4	12.0
	14-63-06	Bxt1	79 - 107	10.2	12.2
	14-63-07	Bxt2	107 - 150	9.7	10.6
	14-63-08	Bxt3	150 - 173	10.2	12.7
	14-63-09	Bxt4	173 - 201	11.9	13.3
	14-63-10	Bxt5	201 - 216	7.0	6.8
	14-63-11	2Bxt6	216 - 239	7.4	5.5
	14-63-12	2Bt1b	239 - 290	7.3	9.9
	14-63-13	2Bt2b	290 - 366	8.9	9.3
Buchanan	31-36-02	A	0 - 5	17.0	16.7
	31-36-03	E	5 - 13	9.3	10.6
	31-36-04	BEt	13 - 23	10.1	12.4
	31-36-05	Bt	23 - 43	12.3	11.0
	31-36-06	Btg1	43 - 66	16.1	18.4
	31-36-07	Btg2	66 - 84	14.1	14.8
	31-36-08	2Bxt	84 - 145	8.8	6.1
	31-36-09	3Bxtb1	145 - 168	6.3	4.6
	31-36-10	3Bxtb2	168 - 185	6.5	5.7
	31-36-11	3Bxtb3	185 - 234	5.5	4.0
	31-36-12	3Bxtb4	234 - 290	6.3	6.3
	31-36-13	3Bxtb5	290 - 330	6.8	5.5
	31-36-14	4BCtb	330 - 363	7.1	8.0
	31-36-15	4Cb	363 - 391	9.3	8.6
	31-36-16	4Crb	391 - 406	11.9	11.8
	Dormont	02-07-02	Ap	0 - 18	17.2
02-07-05		Bt2	48 - 58	10.7	9.1
02-07-08		Bt5	102 - 132	11.1	10.1

Table 3.1. Comparison of Methods of Determining BaCl₂-TEA Extractable Acidity on Selected Pennsylvania Soils.

Soil Series	Soil Number	Horizon	Depth (cm)	-- Extractable Acidity ¹ --	
				pH 8.0 EA ----- meq / 100 g -----	pH 8.2 EA -----
Upshur	02-23-01	Ap	0 - 20	15.3	13.5
	02-23-03	Bt2	41 - 64	23.3	21.5
	02-23-07	C1	117 - 142	6.1	2.8
Bath	08-11-01	Ap	0 - 18	15.9	13.9
	08-11-03	Bw2	28 - 36	11.4	9.9
	08-11-06	Bx3	69 - 107	7.9	6.8
Cookport	17-15-02	BA	5 - 15	26.7	28.9
	17-15-04	Bt2	25 - 38	15.3	14.6
	17-17-07	Bx3	84 - 119	8.6	7.4
Cavode	32-59-01	Ap	0 - 28	12.7	10.6
	32-59-03	Bt1	41 - 53	17.2	16.9
	32-59-06	Cg	119 - 145	11.1	9.5
Lackawanna	45-80-01	Ap	0 - 18	10.2	9.4
	45-80-03	Bw2	36 - 51	4.5	6.1
	45-80-05	Bx1	71 - 135	4.3	5.5
Gilpin (Standard)	14-01-04	Bt	61 - 86	11.2	13.5
	14-01-04	Bt	61 - 86	11.8	10.8
Mean				11.4	11.3
Standard Dev.				5.3	5.4
Standard Error of the Mean				0.76	0.78

NOTE:

1-

pH 8.0 EA = Extractable acidity is determined using a 0.5 N BaCl₂ - 0.055 N TEA extraction/replacement solution buffered at pH 8.0 (Thurman et al., 1992).

pH 8.2 EA = Extractable acidity is determined using 0.5 N BaCl₂ - 0.2 N TEA extraction solution buffered at pH 8.2 and a 0.5 N BaCl₂ replacement solution (SSIS, 1991).

A two sample T-Test found no significant difference (95% confidence interval) between extractable acidity determined by the BaCl₂-TEA, pH 8.0 method (EA_{8.0}) and extractable acidity determined by the BaCl₂-TEA, pH 8.2 method (EA_{8.2}).

Equation for the line that best fits the plot of EA_{8.0} vs. EA_{8.2}:

$$EA_{8.0} = 1.01 + (0.925 \times EA_{8.2}), R^2 = 0.885$$

Recommendations

No significant difference is detected between the BaCl₂-TEA, pH 8.0 method used by the PSUSCL and the BaCl₂-TEA, pH 8.2 method considered the standard method for comparison. No changes are recommended in the PSUSCL procedure for determining extractable acidity.

References

- Ciolkosz, E. J., R. C. Cronce, and R. R. Dobos. 1989. Amorphous material in Pennsylvania soils. Penn State Univ. Agron. Series No. 105.
- Ciolkosz, E. J., and R. R. Dobos. 1991. Pennsylvania State University soil characterization laboratory data summary for standard samples. Penn State Univ. Agron. Series no. 112.
- Ciolkosz, E. J., N. C. Thurman, and R. R. Dobos. 1992. Penn State University soil characterization database system. Penn State Univ. Agron. Dept.
- Hoover, M. T. 1983. Soil development in colluvium in footslope position in the Ridge and Valley Physiographic Province in Pennsylvania. Ph. D. Thesis, Penn. State Univ., Univ. Park, PA. 271 pp.
- Minitab Inc. 1991. Minitab statistical software, release 8. PC version. Minitab Inc. State College, PA.
- Peech, M. 1965. Exchange acidity. p. 905-913 in C. A. Black et al. (Ed.). Methods of soil analysis. Part 2. Chemical and microbiological properties. Agron. No. 9. Amer. Soc. of Agron. Madison, WI.
- Soil Survey Investigations Staff (SSIS). 1991. Soil survey laboratory methods manual. USDA SCS Soil Surv. Invest. Rept. No. 42. National Soil Survey Center. Lincoln, NE.
- Thomas, G. W. 1982. Exchangeable cations. p. 159-165 in A. L. Page, R. H. Miller, and D. R. Keeney (Ed.). Methods of soil analysis. Part 2. Chemical and microbiological properties. Agron. No. 9. (2nd edition). Soil Sci. Soc. of Amer. Madison, WI.
- Thurman, N. C., E. J. Ciolkosz, and R. R. Dobos. 1992. Pennsylvania State University soil characterization laboratory methods manual. Penn State Univ. Agron. Series No. 117.

CHAPTER 4

A COMPARISON OF THE LECO INDUCTION FURNACE AND MODIFIED WALKLEY BLACK METHODS FOR DETERMINING ORGANIC CARBON

Introduction

The Penn State University Soil Characterization Laboratory (PSUSCL) uses the Leco induction furnace to analyze the organic carbon (C) content of most soils (Thurman et al., 1992). This dry combustion method actually determines total carbon (organic C and inorganic carbonates) but in humid regions where the soils have been extensively leached, organic C will be the dominant C form (Nelson and Sommers, 1982). The modified Walkley-Black method is also commonly used to determine organic C. This method oxidizes only organic C and will not overestimate the organic C content when free carbonates are present (Nelson and Sommers, 1982).

In the induction furnace method, organic C is oxidized by dry combustion and reacts with O_2 to form CO_2 . The CO_2 is absorbed in an ascarite bottle, which is weighed to determine the amount of CO_2 collected. In the modified Walkley-Black method, organic matter is oxidized by the dichromate ion ($Cr_2O_7^{2-}$), with sulfuric acid (H_2SO_4) added to provide heat for the reaction. The unreacted $Cr_2O_7^{2-}$ is then determined by titration with a standard Fe^{2+} solution (ferrous sulfate or ferrous ammonium sulfate), and the quantity of oxidizable matter is calculated from the amount of $Cr_2O_7^{2-}$ reduced (Nelson and Sommers, 1982). The organic C is not completely oxidized in this method and a recovery factor of 1.3 is added to the calculations. The presence of oxidizable and reducible constituents, especially Cl^- , Fe^{2+} (overestimations), and MnO_2 (underestimations), can cause interference errors with the procedures (Nelson and Sommers, 1982).

The induction furnace method is simple and rapid, results in complete conversion of organic C to CO_2 , does not require caustic reagents, and provides an accurate assessment of organic C (except when carbonates are present).

A study was conducted by Ciolkosz et al. (1988) to compare the induction furnace method to the modified Walkley-Black method of determining organic C.

Materials and Methods

Four standard samples -- Gilpin Ap (PSUSCL number 02-01-01) and Bt (02-02-02) and Hagerstown Ap (14-01-01) and Bt (14-01-04) -- which had no excess carbonates were selected. The samples were analyzed by the modified Walkley-Black method and by the Leco induction furnace method (Ciolkosz and Cronce, 1986; Ciolkosz et al., 1988).

Results and Discussion

Ciolkosz et al. (1988) found no difference between the Leco furnace and Walkley-Black methods for soils which had no excess carbonates. A summary of the results from the two methods is given in Table 4.1.

For Pennsylvania soils that do not have excess carbonates, organic C is determined by the Leco induction furnace method. For those soils with a $CaCO_3$ equivalent of 1% or higher, the modified Walkley-Black method is used (Thurman et al., 1992).

Table 4.1. A summary of organic carbon data by Leco furnace and modified Walkley-Black methods for soil characterization standard samples.

Standard Soil	Soil No.	Method Used (1)	Number of Analyses	Mean	Standard Deviation
Gilpin Ap	02-01-01	Walkley-Black	8	1.62	0.09
		Leco furnace	9	1.68	0.03
Gilpin Bt	02-01-02	Walkley-Black	8	0.27	0.01
		Leco furnace	8	0.30	0.02
Hagerstown Ap	14-01-01	Walkley-Black	8	1.61	0.06
		Leco furnace	72	1.65	0.06
Hagerstown Bt	14-01-04	Walkley-Black	8	0.11	0.01
		Leco furnace	9	0.17	0.06

NOTE:

(1) Data for organic C by the modified Walkley-Black method are from Ciolkosz et al. (1988). Data for the Leco induction furnace are from Ciolkosz and Cronce (1986).

References

- Ciolkosz, E. J. and R. C. Cronce. 1986. Pennsylvania State University soil characterization laboratory standard sample data summary. Penn State Univ. Agron. Series No. 87.
- Ciolkosz, E. J., R. R. Dobos, and R. C. Cronce. 1988. Pennsylvania State University soil characterization laboratory manual. Penn State Univ. Agron. Series No. 101.
- Nelson, D. W., and L. E. Sommers. 1982. Total carbon, organic carbon, and organic matter. p. 539-579 in A. L. Page, R. H. Miller, and D. R. Keeney (Ed.). Methods of soil analysis. Part 2. Chemical and microbiological properties. Agron. No. 9. (2nd edition). Soil Sci. Soc. of Amer. Madison, WI.
- Thurman, N. C., E. J. Ciolkosz, and R. R. Dobos. 1992. Pennsylvania State University soil characterization laboratory methods manual. Penn State Univ. Agron. Series No. 117.