

AN EVALUATION OF LIME REQUIREMENT TESTS ON PYRITIC MINESOILS¹

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Abstract. Soil samples were collected from 6 abandoned minelands. All were extremely acidic with pH values ranging from 2.79 to 4.51. On each soil, nine lime requirement tests were performed. The tests included the Ca(OH)₂ titration, Woodruff buffer, Mehlich buffer, the Shoemaker, McLean, and Pratt double buffer, KCl exchangeable acidity, acid-base account (total-S), acid-base account (reduced-S), hydrogen peroxide oxidation, and soxhlet extractions. The soils were then incubated in the greenhouse, each with different application rates of a highly reactive limestone. There were five liming rates per soil with each replicated four times. The moisture content was kept at approximately 33 kPa for six weeks followed by two weeks in which water was not added. This cycle continued for 15 months. At the end of six months and twelve months each treatment was leached with 2L of distilled water. The leachate was analyzed for pH. For this paper, only the six month leachate data was available. Incubation-leaching lime requirement values were based on the near maximum reactivity of the limestone. Laboratory values were related to the incubation values through correlation and regression analysis. The Ca(OH)₂ test showed the strongest correlation with the incubation value ($r=.95$). The soil property most closely correlated with the incubation value was total-S ($r=.85$).

Additional key words: Acid-base account, buffer, exchangeable aluminum and pyrite.

Introduction

There are many existing methods which are used to determine the lime requirement (LR) of agricultural soils (Dunn 1943 and Kamprath 1970). Several of the quick-test methods incorporate the use of a buffer solution adjusted to a known pH (Woodruff 1948; Mehlich 1976; McLean et al. 1978). These tests, with

varying degrees of accuracy, account for the active and reserve acidity that results from hydrogen and the hydrolysis reactions of aluminum and its polymers.

Most buffer methods are based on the principle that when a buffer solution of a known pH is mixed with an acid soil the pH will decrease linearly with respect to the H content of the soil.

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The Woodruff (1948) buffer method incorporates the use of a highly buffered solution that has been shown to be accurate on soils with differing exchange capacities and high lime requirements. The Shoemaker, McLean, and Pratt (1961) (SMP) method is ideally suited for soils with significant amounts of exchangeable Al and little organic matter. The SMP double buffer (McLean et al. 1978) (SMPDB) takes into

account the buffering capacity of individual soils. For sandy soils the Yuan (1974) method is often employed while Adams and Evans (1962) devised a buffer for Red-Yellow Podzolic Ultisols.

Numerous comparison studies have been conducted on various types of soils. Alabi et al. (1986) evaluated eight buffer methods on coarse-textured soils of Nebraska. Kenney and Corey (1963) conducted an investigation on 26 Wisconsin soils. Trans and van Lierop (1981) determined the accuracy of buffer methods on Canadian soils. Lateritic soils of India were utilized in a study by Savant and Kibe (1971). When these methods were applied to acidic minesoils Mays and Bengston (1978) have indicated that these methods varied substantially in their prediction of lime requirements. Crews and Vogel (1986) found that the Woodruff and SMP methods underestimate the LR of minesoils containing pyrite.

Often with minesoils there is the added component of acidity generated from the oxidation of pyrite, FeS₂, which yields sulfuric acid (Carruccio 1968 and Smith et al. 1970). The potential acidity from the unoxidized pyrite in the soil fraction must be considered in the total acidity when formulating an LR for these soils.

The acid-base account (Smith 1974) has been a widely accepted method for determining the LR of pyritic materials. The estimation of total S by hydrogen peroxide has also been employed, although it is more suited for fresh overburden material (Sobek et al. 1978).

The objectives of this study were to (1) determine the relationship of LR values predicted by nine methods with those by an incubation-leaching technique based on the maximum reactivity of the limestone, (2) determine the extent of correlation between LR values, and (3) determine the correlation of all LR values with various soil chemical properties. This

is a preliminary report based on the first set of leachate data collected from an ongoing study.

Methods and Materials

Soil Analysis

Samples from six strongly acidic minesoils were collected from abandoned strip mine sites in Monongahela and Preston counties of north central West Virginia. Four sites were completely void of vegetation while the remaining two had little invading vegetation. Samples were collected to a depth of 15 cm. All soils were air-dried at approximately 28 C in the greenhouse and then were passed through a 2 mm sieve. Only the less than 2 mm size fraction was used in the study.

Soil pH was determined with a glass electrode pH meter using a 1:1 soil:water ratio. Organic carbon was determined according to the Walkley-Black method (Allison 1965), cation exchange capacity and exchangeable bases by the NH₄OAc (pH 7) method, and exchangeable acidity and Al by KCl extraction as outlined by the Soil Survey Staff (1984). Moisture retention at 33 kPa of pressure was determined using pressure plates and the pipette method was employed to determine particle size distribution. A Leco induction furnace with an automatic titrator was used to determine percent total - S. Sulfate-S was leached from the samples (Smith et al. 1978) and the percent reduced-S was determined again using the induction furnace. Soil characterization results can be found in Table 1.

Lime Requirement Tests

The Ca(OH)₂ titration (Dunn 1943) in conjunction with a five-minute boiling step, (Abruna and Vincente 1955) was used to determine the lime requirements of all soils. Exchangeable acidity was also used as a basis for liming. Buffer pH methods employed

Table 1. Selected physicochemical measurements of the minesoils.

Measurement	Units	Minesoil Number					
		1	2	3	4	5	6
pH		2.79	2.80	3.36	3.49	4.39	4.51
Organic Matter	%	0.43	0.31	0.20	0.29	0.58	0.47
CEC	cmol/kg	10.50	13.30	9.30	16.20	9.50	8.60
Exch Acidity	cmol/kg	10.93	13.72	9.38	24.57	5.50	10.53
Exchangeable Al	cmol/kg	6.30	6.80	3.70	10.10	1.58	4.60
Total S	%	1.51	0.71	0.13	0.26	0.03	0.07
Reduced S	%	0.41	0.20	0.04	0.04	0.03	0.03
Clay	%	29.00	18.00	24.00	39.00	26.00	39.00

Table 2. Lime requirement determination by various methods.

Measurement	Minesoil Number					
	1	2	3	4	5	6
	Mg/ha					
Ca(OH) ₂	22.06	17.47	12.10	20.38	12.54	14.90
Woodruff	33.50	33.15	23.41	46.66	13.22	18.08
SMP-DB	37.32	28.36	20.76	54.30	13.06	25.56
Mehlich	17.45	18.39	13.69	25.63	7.91	12.97
Ex Acidity	22.56	30.87	23.23	60.50	14.95	25.07
Soxhlets	75.18	31.08	20.65	21.56	9.24	15.12
ABA-TS	124.23	69.78	21.37	38.75	7.71	15.57
ABA-RS	47.17	33.67	15.21	23.27	7.08	12.66
H202	20.14	10.51	3.23	4.95	0.35	4.91
Incubation	34.27	23.74	12.10	24.64	6.50	18.37

included the Woodruff (1948), the Mehlich (1976), and the Shoemaker, McLean and Pratt double-buffer (1978). The acid-base account utilizing both total and reduced-S also served to develop an LR, as was the hydrogen peroxide method. The use of soxhlet extractors (Stiller et al. 1988) was employed to develop an LR based on the sulfate-S concentration in the leachate. Due to time restraints this procedure was conducted after the incubation began. LR values as determined by the various methods can be found in Table 2.

Incubation Procedure

Each soil was limed at five different rates with each rate replicated four times. The rates encompassed the range of LR values as determined by the laboratory tests and can be found in Table 3. Each treatment contained 0.5 kg of soil. Polyethylene containers fitted with rubber spouts were used to contain the soils. The spouts were sealed with polyethylene clamps. Glass wool was used to line the bottom of the containers. A layer of acid-washed sand was placed on top. The soil-lime mixtures were then added. The soils were moistened to approximately 33 kPa for six weeks. This was followed by

two weeks in which no water was added. Alternate wetting and drying periods were chosen to simulate natural conditions. This cycle continued for fifteen months and at the end of the sixth and twelfth months each treatment was leached with 2L of distilled water. This value was chosen in order to remove many of the salts that accumulated during the incubation.

Leachate and Limestone Analysis

The leachate was analyzed for pH with a glass electrode pH meter. The lime used in the study was a pulverised agricultural limestone obtained from German Valley Limestone in Riverton, WV. Total Ca and Mg were determined through atomic adsorption spectrometry. Its CaCO₃ equivalent was determined and its particle-size distribution was defined using 20, 35, 60, 140, 200, 270, and 300 mesh sieves. The activity was derived from a chart for evaluating agricultural limestones devised by Schollenberger and Salter (1943).

Results and Discussion

Lime Requirement Test Comparisons

The correlation coefficients among

Table 3. Incubation lime application rates.

Lime Rate	Minesoil Number					
	1	2	3	4	5	6
	Mg/ha					
1	0	0	0	0	0	0
2	17.0	11.9	6.1	12.3	6.5	10.3
3	34.3	23.7	12.1	24.6	9.6	14.3
4	53.1	32.7	20.2	44.4	13.0	18.4
5	132.8	74.6	25.1	58.0	14.1	27.3

Table 4. Correlation coefficients among laboratory LR values.

Method	WD	SMPD	MEH	ACID	SOX	ABAT	ABAR	H2O2
CA	0.81	0.84	0.80	0.53	0.75	0.81	0.84	0.79
WD		0.94	0.98	0.86	0.41	0.52	0.62	0.44
SMPD			0.97	0.89	0.36	0.43	0.51	0.39
MEH				0.89	0.37	0.46	0.57	0.40
ACID					-0.07	0.03	0.15	-0.03
SOX						0.97	0.93	0.97
ABAT							0.99	0.98
ABAR								0.96

laboratory LR tests can be found in Table 4. The Woodruff, SMP-DB, and Mehlich methods were all significantly related with coefficients > .94. The three buffers were all highly correlated with the Ca(OH)₂ titration and exchangeable acidity as evidenced by coefficients greater than .80. The relationship was not as strong between the Ca(OH)₂ and exchangeable acidity (r=.53). The ABA-TS, ABA-RS, soxhlet extractions, and the H2O2 oxidation were all significantly correlated (r's > .93). These methods all account for the oxidation of residual pyrite. There was a limited relationship between the three buffers and the four sulfur methods as the coefficients ranged from .36 to .62. There was virtually no relationship between these tests and exchangeable acidity (r's < .15). The relationships between the four sulfur tests and the Ca(OH)₂ were strong (r's > .75).

Limestone Analysis Results

The CaCO₃ equivalent was determined to be 96.7%. The calcitic limestone contained 42% Ca and 0.4% Mg. The sieve analysis showed that 100% passed a 60 mesh sieve, 58% a 140 mesh sieve, 35% a 200 mesh sieve, 23% a 270 mesh sieve and 3% passed a 300 mesh sieve. The activity was calculated to be .96, indicating a highly reactive limestone.

Determination of Incubation Leaching LR Values

The LR values were based on the near maximum reactivity of the limestone. This was determined by plotting the leachate pH values for a particular soil against the lime application rates. The plot for soil 1, found in Figure 1, is typical of the results obtained for all soils. All soils reached a point at which increasing rates did not increase the pH significantly. The four most acidic soils reached a peak reactivity with the third liming rate while soils 5 and 6 peaked with the second and fourth rates. Near maximum reactivity pH values ranged from 7.28 to 8.05. They are referred to as near maximum reactivity values

because they are below the theoretical limits on pH for pure CaCO₃.

LR Test Values vs Incubation-Leaching LR Values

Table 5 shows the correlation coefficients and linear regression equations relating the laboratory LR values (LLR) and incubation-leaching LR values (ILR). The regression equations utilized the LLR values as the dependent variables and the ILR values as the independent variable. Regression lines can be found in Figures 2 and 3. If all lab methods were to precisely predict the LRs of the soils the intercept of the equations would be 0 and the slopes would be equal to 1. The data indicates that the intercepts vary from 0 and the slopes are not equal to 1.

The strongest relationship with the ILR was with the Ca(OH)₂ (r = .95). The ABA-RS, H2O2, ABA-TS, and the soxhlet extractions were all significantly correlated with the ILR (r's = .92, .90, .89, and .84). The three buffer tests all exhibited the same strong relationship with the ILR (r = .73). The exchangeable acidity was the least correlated (r = .41). All correlations were significant at the 0.01 probability level except the exchangeable acidity.

Despite having correlation coefficients of similar magnitude the regression equations were substantially different. This may be attributed to the strong possibility of continuing acidification at different rates of the incubated samples due to pyrite oxidation. There are also differences in the nature of the acidity in the soils and in the different abilities of the LLR tests to react with these acids.

In the Ca(OH)₂ test, the base reacts with both acidity in soil solution and on exchange sites. The three buffer solutions react with acidity in a similar manner. They neutralize both solution and adsorbed H ions and also contain displacing cations which remove Al compounds from exchange sites thus allowing for their neutralization with the buffer

Figure 1. Soil 1

Liming rate vs Leachate pH

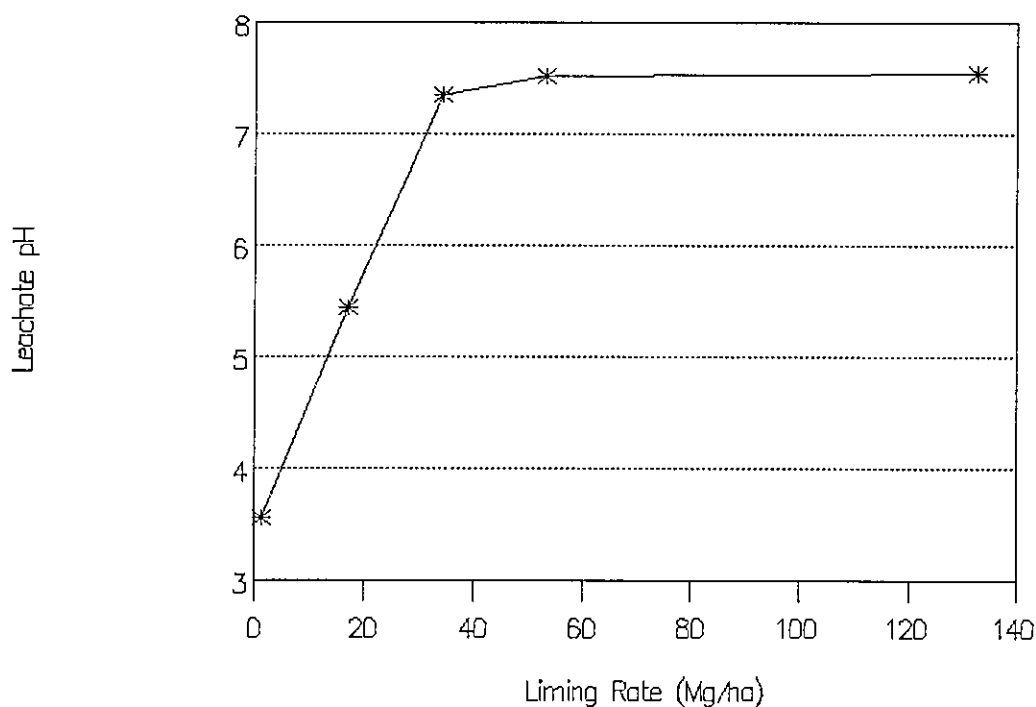


Table 5. Correlations and regressions for Lab LRs vs Inc LRs.

Method	r	Linear Regression Equation
Ca(OH)2	*.95	$y = 8.71 + .39x$
ABA-RS	*.92	$y = -4.67 + 1.4x$
H2O2	*.90	$y = -5.53 + .65x$
ABA-TS	*.89	$y = -32.98 + 3.97x$
Soxhlet	*.84	$y = -11.67 + 2.03x$
Woodruff	*.73	$y = 10.08 + .90x$
SMP-DB	*.73	$y = 8.58 + 1.07x$
Mehlich	*.73	$y = 7.13 + .45x$
Exch. Acid	.41	$y = 12.87 + .24x$

* Significant at the 0.01 probability level.

Figure 2. Fitted Regression Equations

Relating LLR and ILR

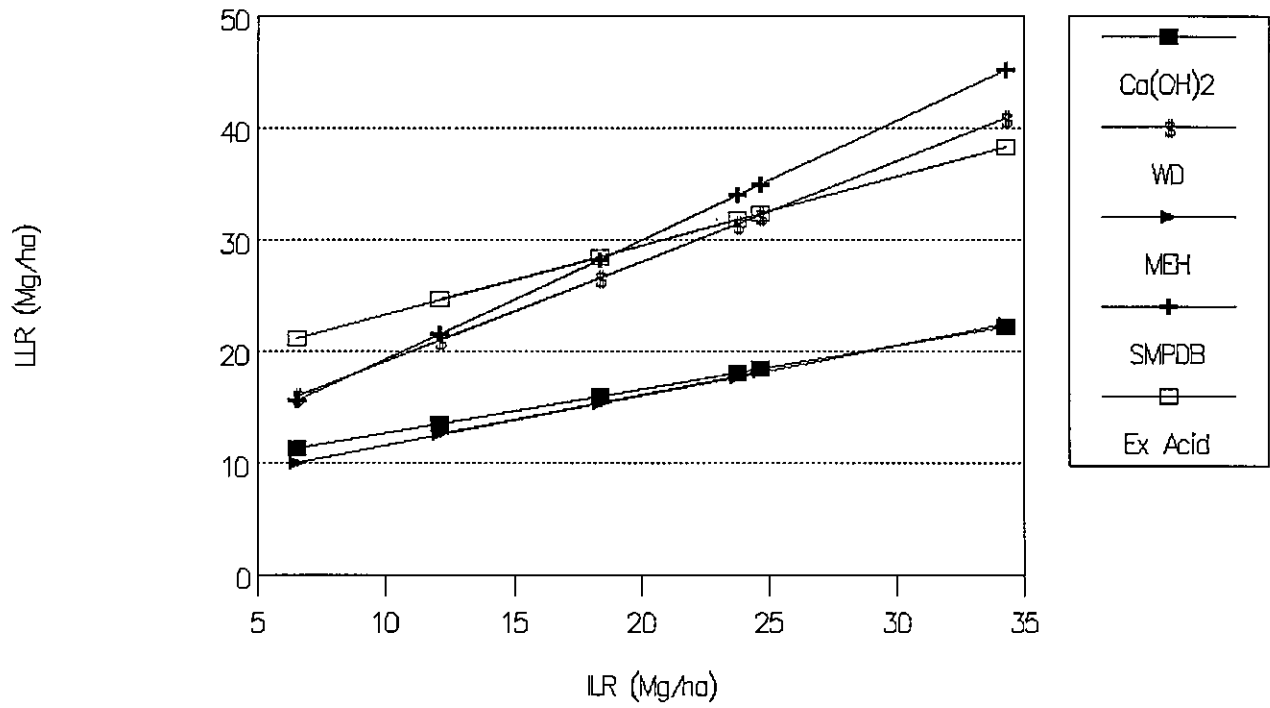
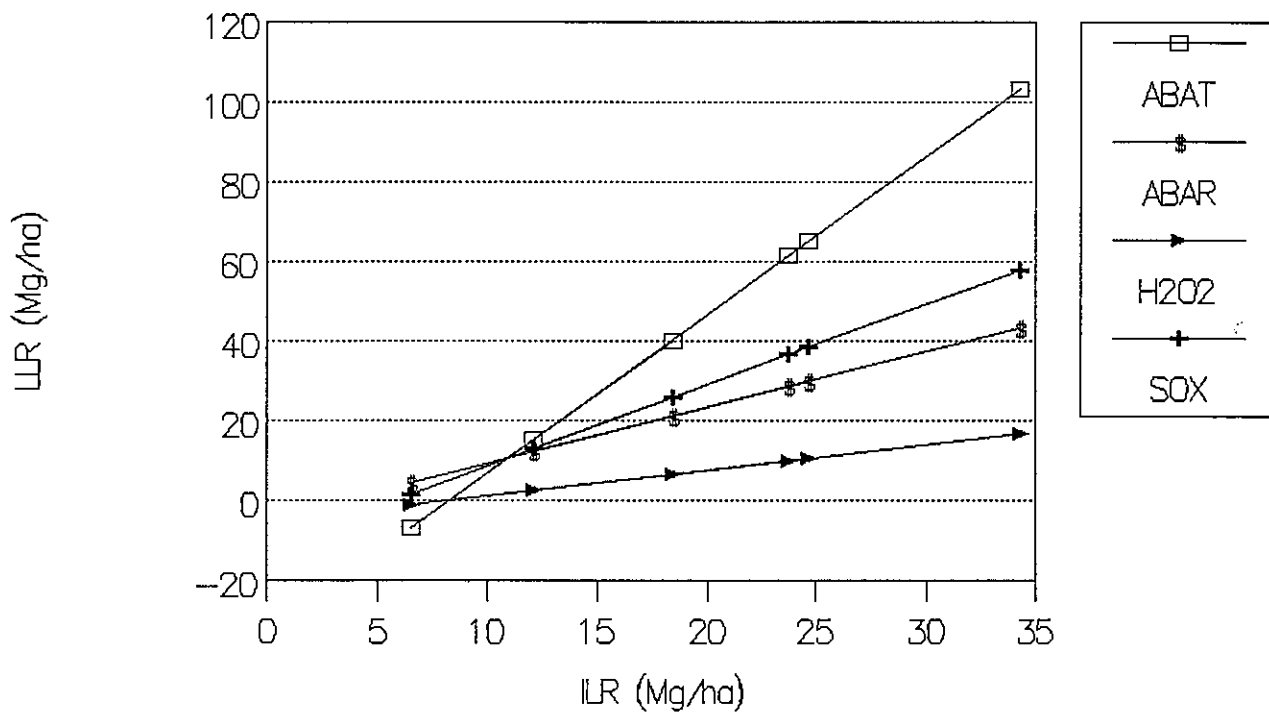


Figure 3. Fitted Regression Equations

Relating LLR and ILR



solutions.

Exchangeable H and Al are displaced by K ions in the KCl extraction method. An amount of CaCO₃ equivalent to the acidity generated from the full hydrolysis of the Al and displaced H in the extract is used as a basis for liming.

The acid-base account balances the maximum potential acidity resulting from the complete oxidation of iron sulfides against a soil's ability to neutralize this acid. Using reduced S measurements to predict the potential acidity, as opposed to total S, is more applicable to weathered minesoils since the SO₄-S will no longer generate acidity. Acidic minesoils quite commonly lack basic minerals which create an intrinsic CaCO₃ equivalent deficit. As a result, free acidity is often detected in determining the neutralization potential. By combining an amount of CaCO₃ equivalent to the total acidity resulting from the complete oxidation of reduced S with an amount needed to neutralize the free acids, an LR is determined. In the H₂O₂ method an LR was based on the potential acidity from pyrite oxidation. Through the use of Soxhlet extractors which simulate geochemical weathering of the minesoils alternate heating and leaching cycles maximize pyrite oxidation. An LR is formulated based on the amount of SO₄-S released.

LLR and ILR Test Values vs Soil Properties

Correlation coefficients of all LR values with selected soil properties can be found in Table 6. The LR values from the three buffer methods and the Ca(OH)₂ titration were significantly correlated with CEC values and levels of exchangeable Al. There was also a strong relationship between CEC and exchangeable acidity (r = .90). The Ca(OH)₂ titration was also highly correlated with total and reduced-S (r = .77 and .70). The four S-tests showed the strongest correlations with levels

of total and reduced-S, and showed strong negative correlations with soil pH. The ILR displayed the strongest correlation with the level of total-S (r = .85).

The reactivity of the limestone may not only have been controlled by the levels of acidity present, but also by the amount of SO₄-S present. The precipitation of gypsum, a CaSO₄ compound, with its subsequent establishment of an equilibrium with the soil solution may have slowed the dissolving of the CaCO₃ due to the common ion effect.

Conclusions

Based on the data available from this study the Ca(OH)₂ LR test was the most strongly correlated with the ILR (r = .95). The four LR tests which accounted for the maximum potential acidity from pyrite were all strongly correlated (r's > .93). There were also strong correlations among the three buffer tests and exchangeable acidity (r's > .86). The four S tests and the buffers were less well correlated. The soil property most strongly correlated with the ILR was total-S (r = .85). The SO₄-S content of the soils appeared to be one of the factors controlling the solubility of the limestone. At the conclusion of the incubation, soil analysis data will be available and additional conclusions will be drawn.

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Table 6. Correlation coefficients of LR values and soil properties.

Method	Clay	CEC	pH	Al	Tot S	Red S
Ca(OH) ₂	0.22	0.82	-0.60	0.58	0.77	0.70
Woodruff	0.18	0.90	-0.66	0.80	0.43	0.33
SMP-DB	0.51	0.93	-0.42	0.91	0.35	0.24
Mehlich	0.33	0.89	-0.57	0.86	0.37	0.26
Exch. Acid	0.48	0.90	-0.21	0.90	-0.06	-0.17
Soxhlets	-0.19	0.41	-0.72	0.05	0.98	0.97
ABA-TS	0.27	0.47	-0.81	0.08	0.99	0.98
ABA-RS	0.26	0.51	-0.86	0.16	0.96	0.94
H ₂ O ₂	-0.19	0.37	-0.73	0.22	0.98	0.97
Incubation	0.13	0.64	-0.69	0.41	0.85	0.79

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