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Organic matter determination of components of high organic matter-sand-soil mixes

David S. Cochran

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To the Graduate Council:

I am submitting herewith a thesis written by David S. Cochran entitled "Organic matter determination of components of high organic matter-sand-soil mixes." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Landscape Architecture.

lloyd M. Callahan, Major Professor

We have read this thesis and recommend its acceptance:

G. Shannon Smith, W. L. Parks, D. B. Williams

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

To the Graduate Council:

I am submitting herewith a thesis written by David S. Cochran entitled "Organic Matter Determination of Components of High Organic Matter-Sand-Soil Mixes." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Ornamental Horticulture and Landscape Design.

Lloyd M. Callahan

Lloyd M. Callahan
Major Professor

We have read this thesis and recommend its acceptance:

C. Shannon Smith

W L Parks

D B Williams

Accepted for the Council:

L Evans Roth

Vice Chancellor
Graduate Studies and Research

A

ORGANIC MATTER DETERMINATION OF COMPONENTS OF HIGH ORGANIC MATTER-SAND-SOIL MIXES

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

David S. Cochran
March 1980

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ABSTRACT

The purposes of this study were (1) to determine the optimum temperature and time period for use with the loss-on-ignition method of organic matter determination, and (2) to compare the effectiveness of the loss-on-ignition method with the Walkley-Black and hydrogen peroxide methods on components of high organic matter-sand-soil mixes.

Three sands and eight organic materials were heated for different time periods at different temperatures. In most cases the organic fraction of these materials were destroyed effectively at 400°C for 6 hours. Ignition at higher temperatures or for longer time periods appeared to introduce error resulting from weight loss from unidentified fractions.

Comparison of the three techniques showed that both loss-on-ignition and the Walkley-Black method have consistent results and both were deemed suitable for the high organic matter-sand rootzone mixes used in the turfgrass industry. Loss-on-ignition is the preferred method, however, due to the need of a correction factor to allow for the consistently low values measured by the Walkley-Black method. Hydrogen peroxide values were quite inconsistent and the method was deemed unacceptable for the materials studied.

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CHAPTER 1

INTRODUCTION

With advancement of technology in Turfgrass Science it becomes increasingly important to accurately characterize specific components within the environment of the grass plant. An important part of this environment is the organic component of the soil supporting turfgrass growth. Organic matter not only is necessary to soil microorganism activity but is essential in the formation of good soil structure and nutrient and water holding capacity of the soil.

Tests for organic matter content of field soils have been investigated for many years. Over the past few years, however, existing soils have often been amended with organic matter in order to improve their physical and chemical properties. On golf greens it has become common practice to construct artificial rootzones by mixing sand and organic amendments. The organic amendment may comprise as much as 20 percent of the total volume of these mixes.

Use of existing methods to accurately determine the percentage of organic matter in these artificial mixes has often proven difficult. Since chemical properties of the freshly added organic amendments are often very different from the humus in natural soils, current methods frequently result in a high degree of error.

The objectives of this study were (1) to compare three presently used organic matter determination methods concerning their applicability for use on the artificial sand-organic matter-soil mixes used on golf greens, and (2) to determine an optimum length of ashing time and temperature for use in the loss-on-ignition method.

CHAPTER 2

REVIEW OF LITERATURE

To accurately characterize a soil by way of laboratory examination necessitates knowing the correct percentage of organic matter present. Organic matter provides the medium required for support of microorganisms, and combined with clay it is responsible for the colloidal properties of the soil (38). A large number of analytical methods for determination of organic matter have been reported (1, 38, 39, 48). Difficulties still persist in choosing the best procedure for accurately determining organic matter due to its complex nature (33). Since errors due to sampling may be 3 to 5 percent, there is little justification for choosing a procedure which gives a degree of accuracy far in excess of the accuracy in sampling. The following methods are the most commonly used in organic matter determinations. Their characteristics will be discussed separately.

I. Loss-on-Ignition Method

The concept of the loss-on-ignition method is based on high temperature ignition of a soil with the organic compounds being oxidized while the inorganic materials remain intact. The difference between the original weight of the soil and the weight of the ash remaining after ignition is considered the weight of the organic matter lost.

According to Ball (6) the usual procedure for determining loss-on-ignition is to weigh a quantity of soil, dry it overnight in an oven at 105°C, reweigh, and ignite in a muffle furnace for 30 minutes at 850°C. Loss-on-ignition is then expressed as the percent of weight lost after the 105°C drying.

A survey of available literature showed considerable disagreement as to what the temperature and time period should be. While Ball (6) recommended 30 minutes at 850°C as the usual procedure he also proposed 16 hours at 375°C. Mitchell (32) reported that 350 to 400°C for eight hours is sufficient while Keeling (24) suggested 375°C for 16 hours. Hesse (20) gave 800 to 900°C for 30 minutes as the usual procedure. Davies proposed a 430°C treatment for 24 hours and Kerr (26) supported a treatment at 300 to 400°C for 30 hours. Wright (52) recommended 700°C for 30 minutes.

Loss-on-ignition is a simple and rapid method of determining organic matter content of soils directly as weight of organic matter (6). Many other methods of determining organic matter are indirect involving a determination of organic carbon in soil. This value must then be multiplied by a factor to give the amount of organic matter. The commonly used factor has been shown to often be in error due to variability of the amount of carbon in soil organic matter (36).

The usefulness of the loss-on-ignition method has been discounted by many researchers due to seemingly inherent errors (6, 33, 38, 47). Waksman (47) said that the error might range from 10 percent in sandy soils to 50 or 70 percent in clay soils. Rather (34) listed these inherent errors as follows: (1) loss of combined water from zeolites, clays, and other hydrated constituents of soil during ignition; (2) loss of carbon dioxide during ignition from calcium carbonate if present in the soil; and (3) oxidation of incompletely oxidized minerals such as ferrous iron compounds during ignition. He stated that the first two errors result in values too high while the third error gives values too low.

There have been several proposals as to how to eliminate these errors. Rather (34) proposed a method whereby he attempted to remove the hydrated and unoxidized minerals and carbonates from the soil before ignition. This was accomplished by successive digestions in an 85°C water bath with a 1 percent acid solution containing 0.5 percent each of hydrochloric and hydrofluric acid, and subsequent washing to remove the acids and their soluble salts. He concluded that this method removed minerals in the soil which interfered with loss-on-ignition while removing only a very small amount of organic matter. This method was further studied and slightly modified by Alexander and Byers (1) who concluded that while the method was relatively accurate it was too slow and expensive for ordinary routine examinations. Read (35) found Rather's loss-on-ignition method useful by incorporating it with the dry combustion method to determine soil organic matter and organic carbon simultaneously.

Another concept for elimination of inherent errors of the loss-on-ignition method was use of a low temperature but longer time period for ignition. Low temperature ignition was performed by Kerr (26) in studies of base exchange of soils. By ignition at 300 to 400°C for 30 hours he was able to destroy the organic matter of the soil without altering the exchange properties of the mineral residue. Kelley et al. (25), also studying base exchange properties of soils, found bentonites and soil colloids remarkably stable at a temperature of 350°C while at 500°C they begin to break down. Mitchell (32) compared the hydrogen peroxide and the ignition methods of destroying soil organic matter and found that ignition at 350 to 400°C for 7 to 8 hours produced a "well-oxidized sample" without destroying or changing the exchange capacity of the inorganic material. In experiments with a number of clays Keeling (24) found that ignition at 375°C for 16 hours removed at least 90 percent of carbonaceous material without removing combined water from the clay itself.

He said that little or no clay breakdown has been shown below 400°C while most carbonaceous materials are known to oxidize below this temperature. Ball (6) evaluated both high temperature (850°C) and low temperature (375°C) loss-on-ignition on noncalcareous soils and compared them to a modification of the Walkley-Black method. He found that correlation between all three techniques was good. He concluded that ignition at both temperatures gave estimates of organic matter which were accurate enough for most uses. He found low temperature ignition to be the most accurate due to the elimination of errors caused by loss of combined water. He concluded that inherent errors of the loss-on-ignition method have been overrated and more consideration should be given to this method.

Davies (15) studied loss-on-ignition of calcareous soils and found that calcium carbonate which was added to the soil did not affect loss-on-ignition when ignited at 430°C for 24 hours. He concluded that loss-on-ignition may be accepted as a gravimetric estimation of soil organic matter in calcareous and noncalcareous soils as long as the ignition temperature is kept between 375 and 450°C. He did point out that there may be an exception in soils containing gibbsite in their clay fraction since gibbsite loses approximately 35 percent of its water around 300°C.

II. Walkley-Black Method

The Walkley-Black method of determining organic matter was introduced in 1934 by A. Walkley and I. Armstrong Black. This method actually measures the reducing power of the soil and makes the assumption that carbon is the chief reducing agent present in soils (50).

As originally proposed the method consisted of treating a sample of soil passing a 0.13 mm sieve with potassium dichromate and strong sulfuric acid. The mixture was then shaken and diluted with water. Sodium fluoride was then added and the chromic acid remaining was titrated with ferrous ammonium sulfate with diphenylamine being used as an indicator (50). Later investigations showed o-phenanthroline-ferrous complex to be a superior indicator (4).

Walkley (48) revised the technique by (1) using soil passing a 0.5 mm sieve, (2) leaving the flask on an asbestos sheet for 30 minutes after digestion and shaking, and (3) titrating with ferrous sulfate rather than ferrous ammonium sulfate. Walkley later determined that the 1 minute shaking was not necessary and results were not changed by varying times of standing between 5 and 40 minutes (49). By this titration method the amount of dichromate which had been reduced could be determined so the amount of carbon which is oxidized could be calculated. One ml of reduced dichromate was equal to 3 mg of oxidized carbon (50).

Walkley and Black based their technique on previous work done by Schollenberger (40) and Degtjareff (17). Schollenberger (40) proposed a method whereby he digested the soil in a potassium dichromate-sulfuric acid solution and heated the mixture to 175°C in 90 seconds. He then added a diphenylamine indicator and titrated with ferrous ammonium sulfate. Degtjareff (17) revised the Schollenberger method. He hypothesized that by adding hydrogen peroxide to potassium dichromate and sulfuric acid he could speed up the oxidation-reduction process. He also simplified the process by allowing the heat of dilution of the sulfuric acid to be substituted for the external heating. Walkley and Black (50) made a study of the Degtjareff method and concluded that the method gave fictitious results. They said the addition of hydrogen peroxide introduced a fundamental error because not only does chromic acid and hydrogen peroxide react with mutual decomposition but the reaction follows a different course with soil than with the blank. While finding the Degtjareff method unsound Walkley and Black did make use of the feature of allowing the heat of dilution of sulfuric acid to suffice for the external heat. Allison (2) reported that 124°C was the maximum temperature reached.

The Walkley-Black method has been found by several researchers to be very good for use in situations where extreme accuracy is not required (5, 44, 48, 50). This method in several peats to be higher than those found by Read and Ridgell. However, the average of 53 percent was still significantly below the accepted 58 percent. Robinson (39) also found the average carbon percentage to be lower than 58 percent with considerable variation among soils with values both above and below 58 percent. Broadbent (10) reported 53 percent carbon in surface soil organic matter and 40 percent carbon in subsoil organic matter. The large variation in carbon percentages of organic matter of different soils and different levels of the same soil provides a very good possibility of significant errors occurring in calculation of organic matter by the Walkley-Black method.

Walkley (48) determined that soils containing considerable amounts of chlorides gave high values for organic matter by the Walkley-Black method. He proposed two alternatives to allow for this. If the amount of chlorides is known a correction can be made by subtracting 1/12 of the chloride content from the apparent carbon content. If chloride content is unknown the chloride may be precipitated by adding silver sulfate. He also found that nitrates of up to 5 percent of the carbon content do not distort results. Manganese dioxide in amounts up to three to four times the carbon content was added without distortion.

has the advantage of being relatively fast and inexpensive. Smith and Weldon (44) reported that the Walkley-Black method was twice as fast and half as expensive as Schollenberger's method and was six times faster and seven times cheaper than the hydrogen peroxide method. Walkley reported that with the Walkley-Black method elemental carbon such as coal or charcoal was practically unattacked thus eliminating that source of error (49). Bremner and Jenkinson (9), however, reported that this method did indeed reflect a variable and significant amount of elemental carbon. Shaw (43) stated that it was very unlikely that there is an oxidizing agent which will oxidize the carbon of soil organic matter without decomposing inert carbonaceous compounds such as coal and charcoal. The presence of carbonates in soil even when they represent 50 percent of the soil did not affect results by this method (5, 27, 49).

While the Walkley-Black method has been recommended for approximate estimations of organic carbon in soil there are several errors which can distort results. This method does not account for all organic matter in a soil. Walkley and Black (50) reported that an average of 76 percent of the organic carbon was accounted for. Actual recoveries varied from 60 to 86 percent. Allison (2) attributes the low and variable recoveries to the low temperature in which the technique is performed. Walkley and Black recommended multiplication by a correction factor of 1.32 to allow for this inherent error. They reported that in soils of similar types, the easily oxidizable organic matter forms a constant fraction of the total organic matter content. Bremner and Jenkinson (8) reported that the Walkley-Black technique gave good results with plant materials and that no correction factor was required.

Browning (11) in a comparison of the Walkley-Black method with the dry combustion method reported an average recovery rate of 85 percent of total organic carbon with considerable variation between soils. Allison (3) got recovery ranging from 59 to 94 percent depending on the particular soil. Variations in recovery were not surprising since the amount of dichromate reduced depends on the type of organic matter present in the soil (11). This variation in recovery introduces an error into the method which cannot be easily accounted for. Piper (33) proposes that rather than introduce error by an often incorrect recovery factor results should be reported as "single value" determinations and designated as "Organic Carbon, Walkley and Black Values." Smith and Weldon (44) also suggest that data be reported as it is found—as milliequivalents of oxidized material per gram of soil. Crowther (14) suggested that if a correction factor is used then a factor should be determined for each group of soils.

White and Holben (51) showed that a chromic acid-sulfuric acid solution will completely oxidize organic matter if the temperature is raised to boiling. Tinsley (46) showed significant thermal decomposition of chromic acid, however, if boiled for 15 minutes in an open flask.

Since the Walkley-Black method determines organic carbon rather than organic matter a conversion factor must be employed to determine the organic matter present. This factor is referred to in much of the literature as the conventional carbon factor. Early in the nineteenth century Sprengel made the statement that soil organic matter averages close to 58 percent in carbon content (42). If this is true then organic matter can be determined by multiplying organic carbon by 1.724 (36, 42). This has been generally accepted and used widely in converting organic carbon values to organic matter values (42). However, this factor has been shown to be inaccurate by several researchers. Read and Ridgell (36) investigated the validity of this factor on a large number of soils from scattered geographical locations. They found the average percentage carbon in organic matter was 49.26 percent for surface soils and 39.16 percent for subsoils and subsurface soils. The percentages of carbon varied from 13.33 to 56.55 percent. In not a single case was the carbon percentage as high as the commonly used 58 percent. Robinson et al. (39) found carbon percentages

Care must be taken when performing the Walkley-Black technique that iron or steel is not introduced into the soil sample. Walkley and Black (50) reported that sufficient metallic iron may be introduced by use of an iron or steel mortar and pestle to cause reduction similar to a significant amount of carbon.

Lee (27) reported that rapid titration methods were not suited to use on water-logged soils. He attributed this to the high reducing potential of the soil due to lack of aeration and to the presence of ferrous iron in the paddy soils he used. Walkley (49), however, found that by air drying such soils for several days good results could be obtained.

Bremner and Jenkinson (8) reported that while the Walkley-Black technique required the assumption that two atoms of oxygen from dichromate are required to oxidize an atom of carbon, this is not always the case. With cellulose the assumption is true but lignins require more than two atoms of oxygen to oxidize a carbon atom, and with proteins less than two oxygen atoms are required. They stated that the requirements of more than two oxygen atoms for lignins and less than two oxygen atoms for proteins seem to cancel so that the assumption of two oxygen atoms per atom of carbon is fairly accurate.

III. Hydrogen Peroxide Method

The hydrogen peroxide method of determining organic matter content in soils was proposed by W. O. Robinson in 1927 (39). This method involves direct determination of soil organic matter by measuring weight loss of a soil which is treated with 15 percent hydrogen peroxide for 1 hour. Hydrogen peroxide acts to destroy or dissolve organic matter while leaving inorganic soil constituents intact (4). Thus the difference in weight before and after hydrogen peroxide treatment can be assumed to be the weight of the organic matter destroyed.

G. W. Robinson and J. O. Jones in 1925 (37) proposed a method whereby hydrogen peroxide was used to determine the degree of humification of soil organic matter. They said that hydrogen peroxide completely oxidizes humified organic matter while leaving intact the fibrous organic substances. In reviewing this work W. O. Robinson (39) found that these findings did not hold true when hydrogen peroxide was added to the organic matter in the presence of soil. He discovered that in the absence of soil cotton fiber and crude fiber were almost unaffected by hydrogen peroxide. However when hydrogen peroxide was added to these materials in the presence of soil they were destroyed almost entirely. He concluded that soil was necessary to catalyze the destruction of the more resistant forms of organic matter and proposed that destruction of organic matter by hydrogen peroxide be used to quantitatively determine the amount of organic matter present in a soil. He said that this method would reflect all except the most resistant carbonaceous material found in most soils.

Robinson's (39) hydrogen peroxide method has received limited support in the literature. Piper (33) stated that the method provided a good measure of organic matter in soils to which it is applicable. He also pointed out an advantage of this method being its slight attack of elemental carbon. Degtjareff (17) pointed out that the Robinson method is simple and convenient but does require an "undue amount of time." Smith and Weldon (44) compared a modification of Robinson's method with three other methods and found that the results from this method were highly correlated with the results of the other three methods. They also pointed out, however, that Robinson's method required the most time and expense of the methods tested.

Several persons have criticized the hydrogen peroxide method of organic matter determination since it is subject to several sources of error. Alexander and Byers (1) investigated Robinson's method and concluded that while the method might be useful for estimating the easily oxidizable matter it was not satisfactory as a means of determining the total organic matter in the soil. Their primary objection was that oxidation is not complete and that the degree of oxidation is not consistent. They showed recovery rates ranging from 73.3 to 89.7 percent. Allison (4) stated similar objections to this method. McLean (29) showed that even with large increases in the amount of peroxide used all the carbonaceous materials could not be oxidized. He also showed that a low concentration of hydrogen peroxide oxidized only the organic matter containing nitrogen while a stronger concentration oxidized at least a part of the more resistant nitrogen-free organic matter. In another paper (30) he showed that above a certain level increasing the strength of the peroxide resulted in little more oxidation of organic matter. In this paper he stated the nitrogenous portion of the organic matter represented 70 to 80 percent of the total organic matter in soil. Waksman and Stevens (47) showed oxidation by hydrogen peroxide ranging from 20.1 percent of sound chestnut wood to 80.2 percent of a peat soil. This work was done in absence of soil, however, and this could be responsible for the low results (1).

Robinson (39) pointed out that the hydrogen peroxide method was not applicable to soils containing more than 2 to 3 percent calcium carbonate or more than a trace of chromium sesquioxide or manganese dioxide. He stated that the latter two are seldom problems since soils containing chromium sesquioxide are rare and soils containing manganese dioxide are usually confined to tropical or subtropical latitudes.

Alexander and Byers (1) reported that manganese dioxide reacted catalytically to decompose hydrogen peroxide and showed that addition of small amounts of acetic acid eliminated this effect. They also showed that pretreatment with hydrochloric acid allowed oxidation of organic matter in soils containing significant amounts of carbonates. They also pointed out the possibility of the hydrogen peroxide oxidizing inorganic materials in the soil resulting in organic matter values which were too low.

Drosdoff and Miles (18) showed evidence of a reaction between weathered mica and hydrogen peroxide resulting in separation of the mica into thin plates and destruction of the hydrogen peroxide. They hypothesized that manganese dioxide, nickel oxide, and chromium oxide in the mica may react with the hydrogen peroxide.

Hosking (21) showed that the hydrogen-ion concentration affected the degree of destruction of organic matter by hydrogen peroxide. He found that under alkaline conditions organic matter was not oxidized to as great a degree as in acid conditions. He attributed at least part of this effect to the greater availability of manganese dioxide in alkaline conditions.

CHAPTER 3

MATERIALS AND METHODS

Studies were conducted to compare the effectiveness of three methods of organic matter determination on eight organic materials and three sands used in high organic matter-sand mixes for golf greens. Studies were also conducted to determine the effects of different temperatures and exposure times by the loss-on-ignition method on the same organic materials and sands. Experiments were conducted from June 1978 to September 1979 utilizing laboratory facilities of the Department of Ornamental Horticulture and Landscape Design of The University of Tennessee.

I. Test Material Preparation

Three different types of sand were selected for this study. A mined, pure silica sand was obtained from White Silica Sand Company in Caryville, Tennessee, and hereafter will be referred to as "white sand" or abbreviated WS. The other two sands were obtained from American Limestone Company in Knoxville, Tennessee. Both were washed sands derived from the Tennessee River. One was a brown color and contained considerable mica and other particulate matter. It will be referred to hereafter as "brown sand" or abbreviated BS.

The other was a yellow sand containing a small quantity of mica and hereafter will be referred to as "yellow sand" or abbreviated YS.

All three sand types were sieved through a 2.00 mm sieve prior to use to remove gravel and debris. Particle size distributions were determined on 100 g samples by the dry sieve method described by Day (16). Silt and clay were determined on 100 g samples by the hydrometer method described by Bouyoucos (7).

Organic materials tested, and their respective assigned abbreviated names, were sewage sludge (SS), Michigan peat (MP), sphagnum peat (SP), oak sawdust (OS), pine bark (PB), corn stalk (CS), cotton stalk (CT), and soybean stalk (SB). Sphagnum peat, pine bark, and Michigan peat were obtained from local garden stores. Oak sawdust was obtained from a local sawmill. Sewage sludge was obtained from the Knoxville Third Creek Waste Disposal Plant. Cotton stalks, corn stalks, and soybean stalks were obtained from 1978 crops grown on The University of Tennessee Plant Sciences Farm in Knoxville. All organic materials were oven dried at 105°C and were then shredded in a Wily mill until they passed a 1 mm sieve to insure uniform size. Each test sample was stored in a large paper bag in a dry location. All test materials were oven dried at 105°C for at least 24 hours prior to use.

II. Sample Size

The relative sample size of each organic material represented the amount of that amendment which would be found in a mix which was 80 percent white sand and 20 percent organic matter by volume. Since precise and accurate volumetric measurements are not conveniently performed in the laboratory, a conversion from volume to weight was made by establishing the density of each material. The weight of each organic material required to give a mix which was 80 percent sand and 20 percent organic matter by volume could then be easily calculated. Samples of the same weight were used for all three sands since their densities were similar.

Sample weights of each material tested were not the same for each of the methods of organic matter determination due to the different requirements of each method. Sample weights for each method are reported in Table 1.

III. Determination of Test Material Densities

Density measurements were made by weighing the amount of material which occupied a volume of 500 ml while subjected to a pressure of 0.211 kg/cm^2 (3 PSI). A 1.9 cm thick piece of wood was cut and sanded to barely fit inside a 600 ml glass beaker. The wood block had a diameter of 8.3 cm. The tared beaker was filled with the material being tested to above the 500 ml mark and the top surface was leveled. The

Table 1. Test material densities and sample weights used for each method of organic matter determination.

	Density g/cc	Loss-on-Ignition g	Walkley-Black g	Hydrogen Peroxide g
White Sand	1.416	50.000	5.000	5.000
Brown Sand	1.332	50.000	5.000	5.000
Yellow Sand	1.502	50.000	5.000	5.000
Oak Sawdust	0.250	1.900	0.190	0.190
Sphagnum Peat	0.132	1.000	0.100	0.100
Michigan Peat	0.427	3.200	0.320	0.320
Pine Bark	0.515	3.900	0.390	0.390
Sewage Sludge	0.687	5.100	0.510	0.510
Soybean Stalk	0.248	1.900	0.190	0.190
Cotton Stalk	0.250	1.900	0.190	0.190
Corn Stalk	0.157	1.200	0.120	0.120

wood block was then carefully placed on the surface of the material. After the block was in place, a 11.123 kg (24.5 lbs) force was gently applied to the center of the top surface of the wood block by a modified impactor similar to the one described by Bruce (12). The impactor was built by Jellicorse (22) and was modified by this researcher by removing the sliding 1.362 kg (3 lbs) weight and replacing it with weights to bring the total weight of the shaft, base, and weights to 11.123 kg. This resulted in a pressure of 0.211 kg/cm^2 being exerted by the wood block on the test material. If the test material did not exactly fill the 500 ml volume when compacted, material was added or removed until the 500 ml volume was exactly filled. Once the proper level was attained the wood block was removed and any test material sticking to it was brushed into the beaker. The beaker and contents were then weighed. By subtracting the weight of the beaker from the total weight, the weight of material occupying 500 ml when under 0.211 kg/cm^2 of pressure was accurately determined.

IV. Loss-on-Ignition Method

Loss-on-ignition was determined by the procedure described by Ball (6). This involved oven drying the test material at 105°C for at least 24 hours, placing an accurately weighed sample in a porcelain ashing dish, and heating in a muffle furnace for a specified period of time at a specified temperature. The furnace was heated to the desired temperature before the dishes and samples were placed inside. Because the oven cooled somewhat when the door was opened to place the samples inside, timing did not begin until the desired temperature was again reached. The difference between the oven dry weight of the sample and the weight of the ash after heating was reported as loss-on-ignition. Loss-on-ignition was considered to be the organic matter which was destroyed.

Quadruple determinations of each test material were heated at temperatures of 200, 300, 400, 500, 600, 700, and 800°C for 1.5 hours for comparison with results of the other two methods of organic matter determination. In addition, a study was conducted to determine the effects of different time exposures and temperatures of the loss-on-ignition method on each test material. In this segment of the study four replications of each test material were heated for time periods of 0.75, 1.5, 3.0, 6.0, 12.0, and 24.0 hours at temperatures of 200, 400, 600, and 800°C. Sample weights tested are reported in Table 1.

Organic material sample sizes for the loss-on-ignition tests were determined as if they were components of a 50 g sample which was 20 percent organic amendment and 80 percent white sand. A 50 g basis was used to insure that all test samples were large enough for accurate weighing. Fifty g samples of the three sands were tested also.

V. Walkley-Black Method

Easily oxidizable organic matter was determined on quadruple determinations of each test material by the Walkley-Black method as described by Allison (4). Sample weights tested are reported on Table 1 (page 22). This method involved oxidation of organic matter by potassium dichromate in the presence of water and sulfuric acid. The solution was then titrated with ferrous sulfate to determine the amount of potassium dichromate reduced. Each milliequivalent of potassium dichromate reduced represented three milligrams of carbon which was oxidized. This resulted in the use of a multiplication factor of 1.724. Sand samples were not ground to pass through a 0.50 mm sieve due to the large amount of coarse sand particles in the brown and yellow sands.

Organic material sample sizes were not based on a one gram sample as recommended by Allison (4). They were determined as if they were components of a 5 g sample of a mix which was 20 percent organic amendment and 80 percent white sand by volume. This avoided the use of extremely small samples of organic materials which could not be accurately weighed. Five g sand samples were tested also.

Because many samples contained more organic matter than called for in the procedure according to Allison (4), the amounts of water, potassium dichromate, sulfuric acid, and indicator solution were increased accordingly. These reagents were added in amounts which resulted in no more than 80 percent of the available potassium dichromate being reduced by the organic matter (4).

Percent organic matter by the Walkley-Black method was calculated by the following formula:

$$\frac{(\text{meq. } K_2Cr_2O_7 - \text{meq. Fe } SO_4) \times 3 \times 1.724 \times 100}{\text{mg of oven dry sample}} = \text{\% organic matter.}$$

VI. Hydrogen Peroxide Method

Percent organic matter by the hydrogen peroxide method described by Robinson (39) was determined on quadruple determinations of each test material. Sample weights tested are reported in Table 1 (page 22). Thirty percent hydrogen peroxide mixed with an equal part of distilled water was used to destroy organic matter in the samples. Digestion was carried out on a hot plate calibrated at 90°C for 3 hours for all tests. This was three times longer than the one hour Robinson (39) said would take care of most soils. The digestion residue was then filtered, oven dried, and weighed. The filtrate was collected in a tared 100 ml glass dish, evaporated, and ignited at 680°C for a period of 1.5 hours.

After the dish and ash came to equilibrium with the moisture in the atmosphere they were accurately weighed. The sum of the digestion residue weight plus the weight of the ash from the filtrate was considered to be inorganic constituents of the sample. The hydrogen peroxide used in this test was determined to have a residue after evaporation and ignition of 0.030 g/50 ml. This factor was subtracted from the total of the digestion residue plus ash from the filtrate. The following equation was used to calculate percent organic matter by the hydrogen peroxide method:

$$100 - \frac{(\text{digestion residue} + \text{filtrate ash}) - 0.030 \text{ g} \times 100}{\text{oven dry sample (g)}} = \% \text{ O.M.}$$

Sample sizes of organic amendments were determined as if they were components of a 5 g sample of a mix which was 20 percent organic amendment and 80 percent sand by volume. This resulted in sample sizes near the 200 mg size recommended by Robinson (39) for organic soils and peat. Five g sample sizes of the three sands were tested. Since the tests were run on the basis of a 5 g sample rather than 1 g as suggested by Robinson (39), 50 ml of hydrogen peroxide was used rather than the 10 ml called for in the procedure.

CHAPTER 4

RESULTS AND DISCUSSION

Studies were conducted to compare three commonly used organic matter (combustible or digestible fraction) determination methods and their effectiveness on eight organic materials and three sands. An additional objective was to determine the lowest temperature and shortest time period to be used with the loss-on-ignition method. The results of the optimum time and temperature determinations were compared with those of the Walkley-Black and hydrogen peroxide methods. A characterization of the sands was conducted by fractional analysis, hydrometer tests, and x-ray diffraction.

I. Characterization of Sands

Ignition

White, yellow, and brown sands showed some similarities in responses to changes in ignition temperature. All three sands showed an increasing percent loss as temperature was increased from 200 to 800°C (Figures 1, 2, and 3). All three sands showed large increases in loss-on-ignition when the temperature was raised from 400 to 600°C. However, the yellow and brown sands exhibited the presence of a greater

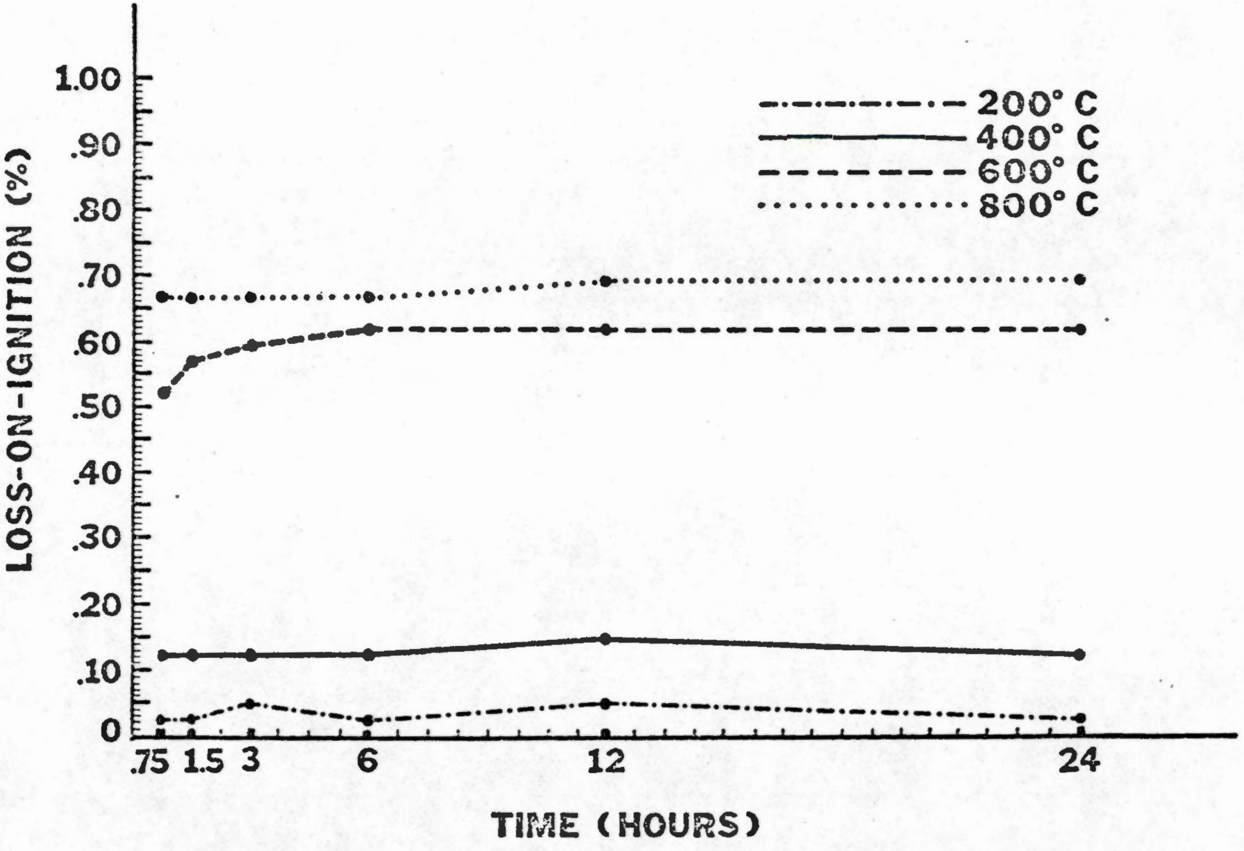

Figure 1. Loss-on-ignition of white sand when ignited at different temperatures and times.

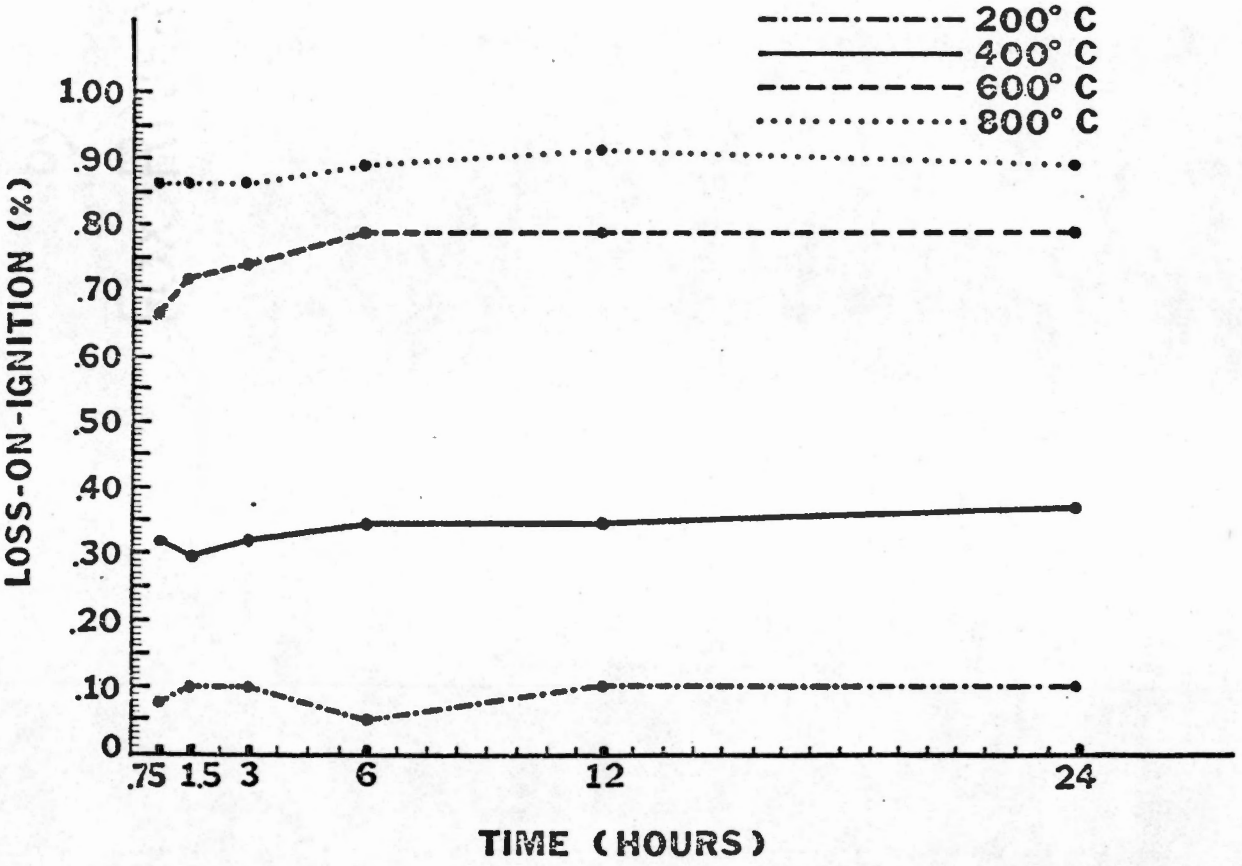

Figure 2. Loss-on-ignition of yellow sand when ignited at different temperatures and times.

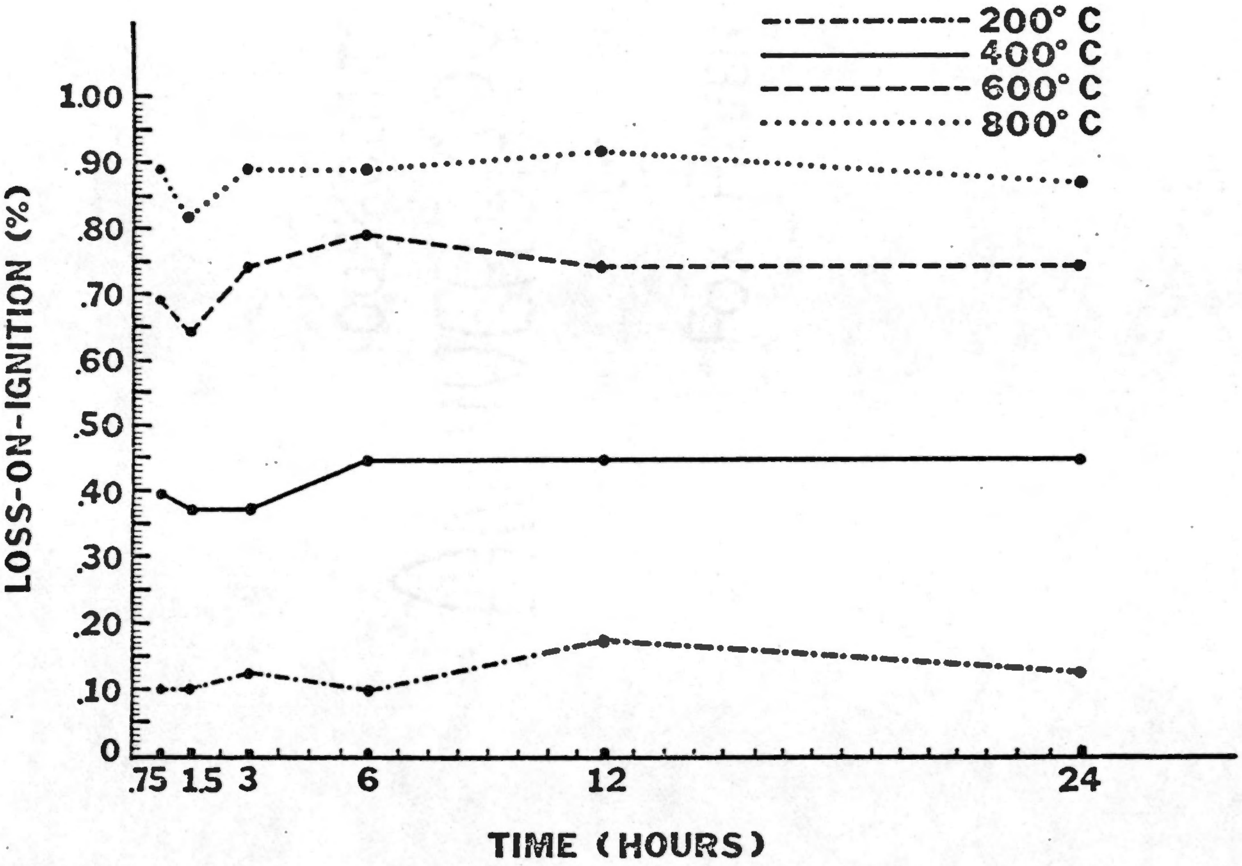

Figure 3. Loss-on-ignition of brown sand when ignited at different temperatures and times.

amount of combustible material that could be lost at each of the four temperatures than did the white sand. The highest loss shown was by the yellow sand with a loss of 0.92 percent at 800°C for 6 hours (Figure 2 and Table 2).

The three sands were ignited at the additional temperatures of 300, 500, and 700°C, but for only 1.5 hours, in order to develop a more complete understanding of their response to increasing ignition temperature ranges (Figure 4). White sand again clearly showed a presence of less combustible material than the yellow and brown sands at each of the seven ignition temperatures. All three sands exhibited a sigmoid type curve that increased in percent loss-on-ignition as temperatures increased from 200 to 800°C. White and yellow sand showed a steep curve increase between 400 and 600°C and a slight increase between 600 to 800°C. Brown sand showed a very slight to almost linear curve increase from 200 to 700°C then leveled off to 800°C. The maximum ignition loss from white sand was 0.71 percent and 0.92 percent for the yellow sand (Table 2). With the sharp increases in the curve generally occurring as temperatures increase above 400°C, results tend to indicate that errors in the procedure could increase significantly as ignition temperatures exceed 400°C. Ball (6) stated that most of the water loss of clay minerals occurred between 450 and 600°C. Keeling (24) observed that differential thermal and thermogravimetric curves of clays

Table 2. Mean percent weight loss of three sands heated at different temperatures for different time periods.

		Percent Weight Loss[1]		
Temp (°C)	Time (Hrs)	Brown Sand	White Sand	Yellow Sand
800	24.00	0.87 e	0.70 c	0.91 b
800	12.00	0.91	0.71	0.92
800	6.00	0.91	0.68 d	0.90 d
800	3.00	0.90 b	0.69 d	0.89 e
800	1.50	0.82	0.67	0.87
800	0.75	0.90 b	0.68 d	0.88
700	1.50	0.84	0.66	0.82
600	24.00	0.74	0.63	0.81
600	12.00	0.75	0.63	0.80
600	6.00	0.80	0.63	0.79
600	3.00	0.74	0.60	0.74
600	1.50	0.66	0.58	0.72
600	0.75	0.70	0.54	0.66
500	1.50	0.53	0.34	0.53
400	24.00	0.44	0.13	0.37
400	12.00	0.45	0.14	0.36
400	6.00	0.44	0.13	0.34
400	3.00	0.39	0.11	0.33
400	1.50	0.39	0.12	0.31
400	0.75	0.39	0.12	0.33
300	1.50	0.28	0.09	0.24
200	24.00	0.12	0.03	0.10
200	12.00	0.16	0.05	0.11
200	6.00	0.10	0.03	0.06
200	3.00	0.12	0.04	0.09
200	1.50	0.10	0.03	0.09
200	0.75	0.11	0.04	0.07

[1] Underlined = maximum weight loss.
b = at least 98% of maximum weight loss.
c = at least 97% of maximum weight loss.
d = at least 96% of maximum weight loss.
e = at least 95% of maximum weight loss.

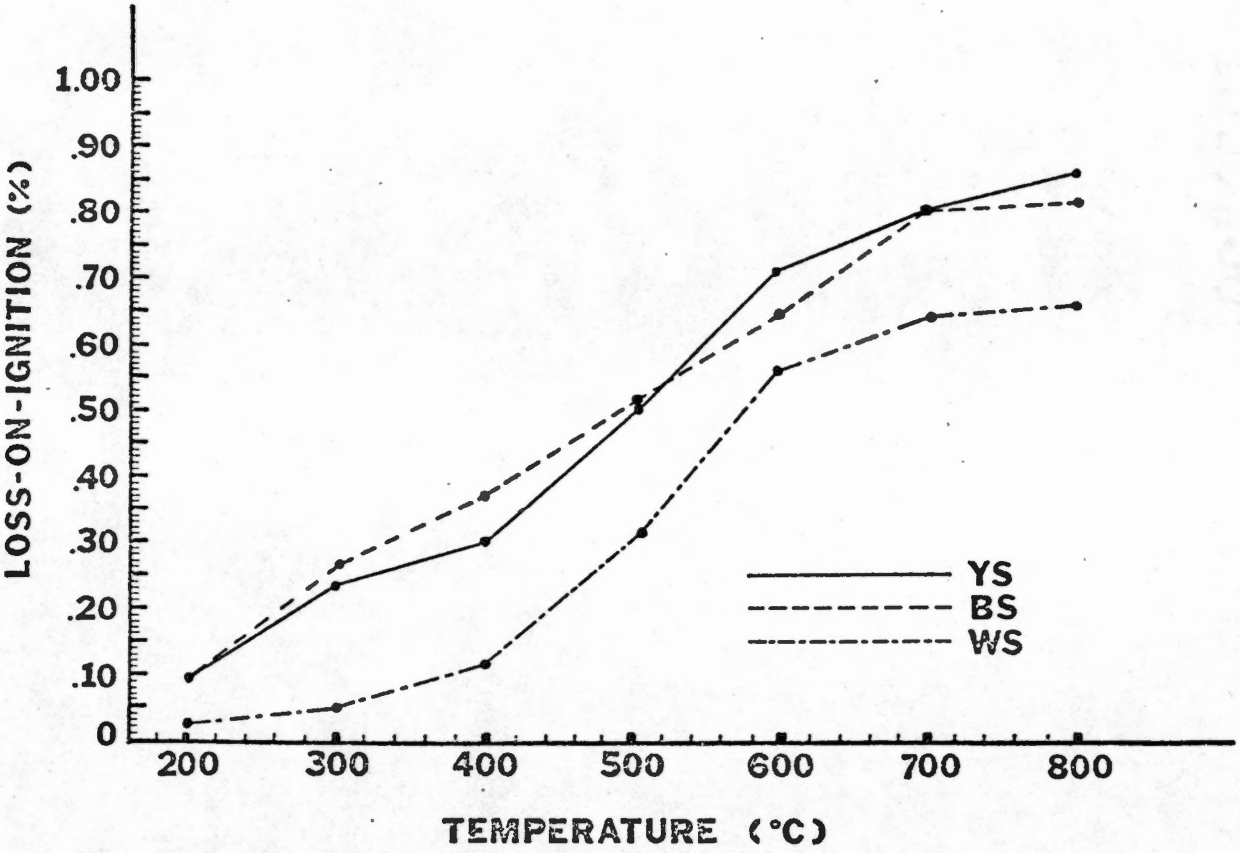

Figure 4. Loss-on-ignition of three sands when ignited at different temperatures for 1.5 hours.

show little or no breakdown below 400°C. Thus loss of combined water from clay contaminating the sands might explain the sharp rise in ignition loss from 400 to 600°C.

All the sands reacted similarly to changes in the time period for which ignition was performed. There was a general increase in the ignition loss at each temperature as the time period was increased (Figures 1, 2, and 3). These increases were variable, however, and in several instances there actually were decreases in loss-on-ignition where the time period at a given temperature was increased. This can be seen with white sand (Figure 1) at 200°C, yellow sand (Figure 2) at 200 and 400°C, and brown sand (Figure 3) at 600 and 800°C. These inconsistencies were small values in most cases and are attributed to experimental error.

While there was a general tendency for the weight loss to increase as the time period was increased, the increase was relatively small in comparison to that derived from increases in temperature of ignition. Analysis of variance showed significant time effects and temperature effects for each of the sands. Time period effects were of much smaller magnitudes, however, than temperature effects. The F values of the time period effects for brown sand, white sand, and yellow sand were 51.33, 99.20, and 216.41, respectively. The F values of the temperature effects were much greater being 10,770.37, 76,968.19, and 68,119.03, respectively.

This indicated that the greatest portion of the variation in loss-on-ignition was due to varying temperature. Thus, while there was a significant effect manifested by changes in ignition time period, the portion of the total variation in loss-on-ignition which can be attributed to changes in time period was relatively small.

Particle Size Distribution

Silt-clay determinations by the hydrometer method (7) were performed on four samples of each of the sands and a mechanical analysis conducted on the sand fractions. Determinations showed the total sand percentage of the three sands to be fairly similar. Total percent of sand in the three sands were 93.5, 96.2, and 94.7 percent for brown sand, yellow sand, and white sand, respectively (Table 3). The remaining portions were silt and clay sized particles. All three sands contained similar amounts of clay ranging from 2.4 to 3.0 percent. Silt percentages varied slightly more ranging from 1.5 to 4.0 percent.

Fractional analysis by the dry sieve method (16) was performed on four replications of each sand. Due to differences in this method and the hydrometer method the total percentages of sand and nonsand particles reported by the two methods may differ. Fractional analysis showed brown sand to be the coarsest with the vast majority of the particles falling in the coarse and medium size fractions (Table 3).

Table 3. Particle size distribution of the three sands.

Size Fraction	mm	White Sand %	Brown Sand %	Yellow Sand %
Very Coarse	(1.000-2.000)	0.92	4.45	6.22
Coarse	(0.500-1.000)	3.04	54.49	15.01
Medium	(0.250-0.500)	44.69	39.30	27.52
Fine	(0.100-0.250)	41.72	1.57	34.24
Very Fine	(0.050-0.100)	4.57	0.05	13.69
Silt	(0.002-0.050)	2.3	4.0	1.4
Clay	(< 0.002)	3.0	2.5	2.4

Only small amounts of the particles fell in the remaining size fractions. Yellow and white sand both showed a predominance of particles in the medium and fine ranges. White sand contained few particles in the other ranges, however, yellow sand contained considerable amounts in the coarse and very fine ranges.

X-ray Diffraction

X-ray diffraction tests were run on each of the sands in order to identify any crystalline minerals which might be present. Results indicated white sand to be primarily quartz and containing no measurable crystalline impurities. Brown sand was found to be primarily quartz but also contained micaceous materials, goethite, and feldspars. Yellow sand also was primarily quartz with a small amount of feldspars.

Review of literature concerning the thermogravimetric properties of these materials showed that neither quartz nor feldspars show significant weight loss over the temperature ranges used in this study (45). Micaceous materials differ in their thermogravimetric properties (31). Some micas such as talc and lepidolite lose little weight over the temperatures used in these studies. However, other micas such as muscovite and prochlorite begin losing weight between 400 and 600°C and show increasing weight loss as the temperature is raised above 800°C. Total weight losses are about 5 percent for muscovite and 10 percent for prochlorite.

Hydrous micas such as celadonite, vermiculite, illite, vermiculite-chlorite and jeffersite lose weight at relatively low temperatures. Most of these begin losing weight at around 100°C with considerable weight loss by 200°C. Their weight loss then levels off and a second increment of loss occurs between 400 and 700°C. The total weight losses for the hydrous micas vary from 5 to 14 percent. Most are in the 5 to 8 percent range. Goethite begins losing weight at about 100°C and loses about 13 percent of its weight at 400°C (28).

II. Characterization of Organic Materials

Loss-on-ignition showed close similarities between five of the eight organic materials. Corn stalk, cotton stalk, soybean stalk, oak sawdust, and sphagnum peat all showed maximum ignition losses of at least 98.82 percent (Tables 4 and 5). These materials sustained very small weight losses when heated to 200°C. Corn stalk showed the largest weight loss at that temperature with a loss of 14.67 percent. The losses ranged down to a minimum of 0.53 percent when soybean stalk was heated to 200°C for only 0.75 hours. The five organic materials showed very large increases in loss-on-ignition when the temperature was raised from 200 to 300°C (Tables 4 and 5). The least amount that any one of these five organic materials lost at 300°C was 74.84 percent for

Table 4. Mean percent weight loss of corn stalk, cotton stalk, oak sawdust, and soybean stalk heated at different temperatures for different time periods.

Temp (°C)	Time (Hrs)	Percent Weight Loss[1] Corn	Cotton	Oak	Soybean
800	24.00	98.46 a	98.61 a	99.03 a	98.47 a
800	12.00	97.83 b	98.18 a	99.20	98.33 a
800	6.00	98.40 a	98.57 a	99.05 a	98.84 a
800	3.00	99.06	98.82	98.79 a	99.32
800	1.50	97.88 b	98.36 a	98.86 a	98.91 a
800	0.75	97.48 b	97.97 a	99.11 a	98.42 a
700	1.50	98.19 a	98.03 a	98.76 a	98.83 a
600	24.00	97.83 b	98.20 a	98.84 a	98.88 a
600	12.00	97.54 b	98.82	98.82 a	98.62 a
600	6.00	98.25 a	97.88 a	98.99 a	98.66 a
600	3.00	97.79 b	97.76 b	98.51 a	98.49 a
600	1.50	97.42 b	97.66 b	98.53 a	98.46 a
600	0.75	98.21 b	97.59 b	98.45 a	98.55 a
500	1.50	97.73 b	97.58 b	98.54 a	98.00 a
400	24.00	97.25 b	97.49 b	98.21 a	97.91 b
400	12.00	97.02 c	97.25 b	98.25 a	97.97 b
400	6.00	96.88 c	97.22 b	97.46 b	97.57 b
400	3.00	97.04 b	96.53 c	97.76 b	95.33 e
400	1.50	96.04 d	95.00 d	96.34 c	95.68 d
400	0.75	93.04	93.71	94.63 e	91.71
300	1.50	80.42	78.54	74.84	82.67
200	24.00	14.67	8.04	11.00	11.38
200	12.00	5.13	8.16	8.53	7.71
200	6.00	7.63	7.92	1.57	4.68
200	3.00	3.06	2.25	2.55	2.49
200	1.50	4.33	1.99	1.49	2.17
200	0.75	0.77	0.65	1.51	0.53

[1] Underlined = maximum weight loss.
a = at least 99% of maximum weight loss.
b = at least 98% of maximum weight loss.
c = at least 97% of maximum weight loss.
d = at least 96% of maximum weight loss.
e = at least 95% of maximum weight loss.

Table 5. Mean percent weight loss of Michigan peat, pine bark, sphagnum peat, and sewage sludge heated at different temperatures for different time periods.

		Percent Weight Loss[1]			
Temp (°C)	Time (Hrs)	Michigan Peat	Pine	Sphagnum Peat	Sewage Sludge
800	24.00	87.43 b	60.79	98.63 a	47.48 b
800	12.00	88.90	69.38	99.18 a	47.09 b
800	6.00	88.13 a	62.74	98.85 a	47.37 b
800	3.00	87.28 b	61.49	98.93 a	48.02
800	1.50	87.59 b	58.90	99.20 a	47.19 b
800	0.75	86.90 c	61.17	98.90 a	45.59
700	1.50	86.98 c	59.04	99.10 a	40.78
600	24.00	87.71 b	58.90	98.68 a	39.41
600	12.00	88.46 a	67.71 c	99.60	37.37
600	6.00	86.79 c	57.10	99.23 a	36.86
600	3.00	86.64 c	59.05	98.83 a	36.09
600	1.50	86.56 c	57.41	99.03 a	35.22
600	0.75	77.59	63.68	99.05 a	35.96
500	1.50	86.02 d	58.24	98.63 a	33.97
400	24.00	85.73 d	57.24	98.60 a	33.40
400	12.00	86.60 c	64.30	98.85 a	32.64
400	6.00	85.56 d	56.78	97.60 b	32.73
400	3.00	85.14 e	57.22	97.28 c	32.11
400	1.50	80.74	53.21	94.13	31.52
400	0.75	74.63	49.94	96.10 d	30.18
300	1.50	82.45	53.53	75.88	25.76
200	24.00	12.20	9.13	8.15	6.68
200	12.00	6.56	6.58	13.73	4.93
200	6.00	6.04	3.32	4.98	2.32
200	3.00	3.71	2.93	2.70	2.04
200	1.50	2.69	1.81	2.20	2.38
200	0.75	3.91	1.60	2.85	0.70

[1] Underlined = maximum weight loss.
a = at least 99% of maximum weight loss.
b = at least 98% of maximum weight loss.
c = at least 97% of maximum weight loss.
d = at least 96% of maximum weight loss.
e = at least 95% of maximum weight loss.

oak sawdust. When the temperature was raised from 300 to 400°C there was considerable additional loss of combustible materials but raising the temperature from 400 to 600°C showed little to no additional loss. This agreed with the results of Keeling (24) who found that ignition at 375°C for 16 hours destroyed at least 90 percent of the carbonaceous material. Further increase in the ignition temperature to 800°C resulted in only slight increases in the loss-on-ignition. Figure 5 shows additional data for weight losses at 100°C increments when heated for a 1.5 hour duration. The graphical plots of the five organic materials listed above fall almost directly on top of each other. Each showed a sharp increase in loss-on-ignition when the temperature was raised from 200 to 300°C followed by another sharp increase when the temperature was raised from 300 to 400°C. All of the materials showed very little increase in ignition loss when the ignition temperature was raised at 100° increments from 400 to 800°C.

Increases in the time period of heating resulted in general increases in weight losses when the temperature was 200°C. The increases for oak sawdust (Figure 6) and soybean stalk (Figure 7) were relatively consistent. Cotton stalk (Figure 8) increased until the duration was 6 hours and then remained about the same as the time was increased further. Sphagnum peat (Figure 9) and corn stalk (Figure 10) showed

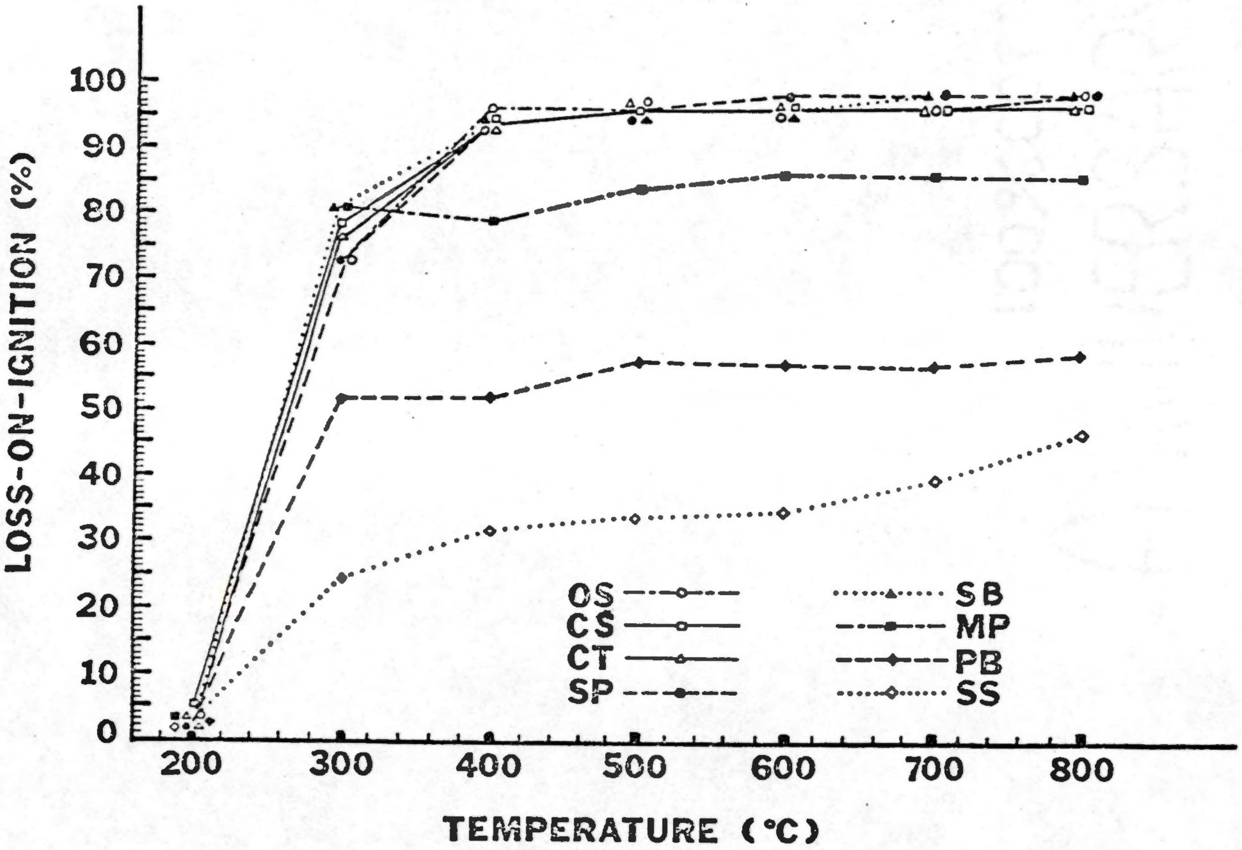

Figure 5. Loss-on-ignition of eight organic materials when ignited at different temperatures for 1.5 hours.

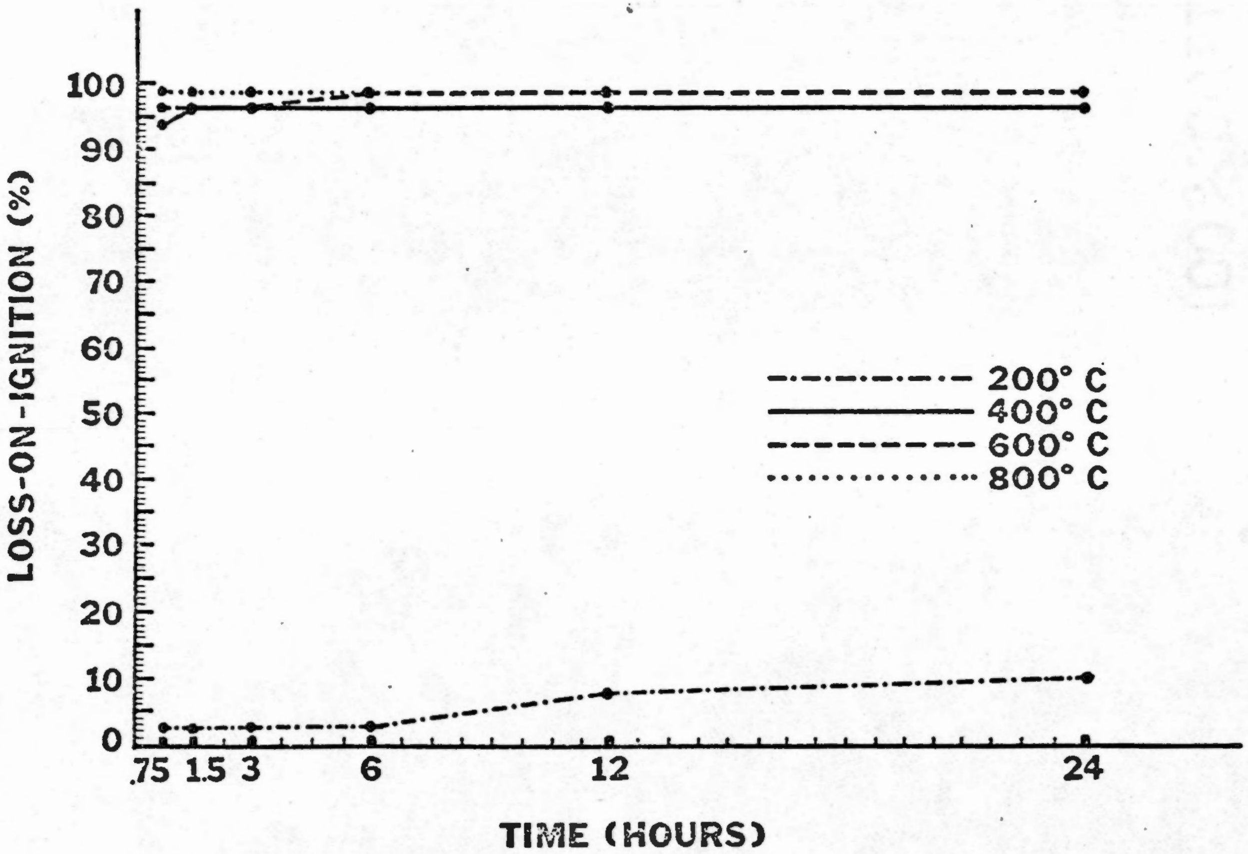

Figure 6. Loss-on-ignition of oak sawdust when ignited at different temperatures and times.

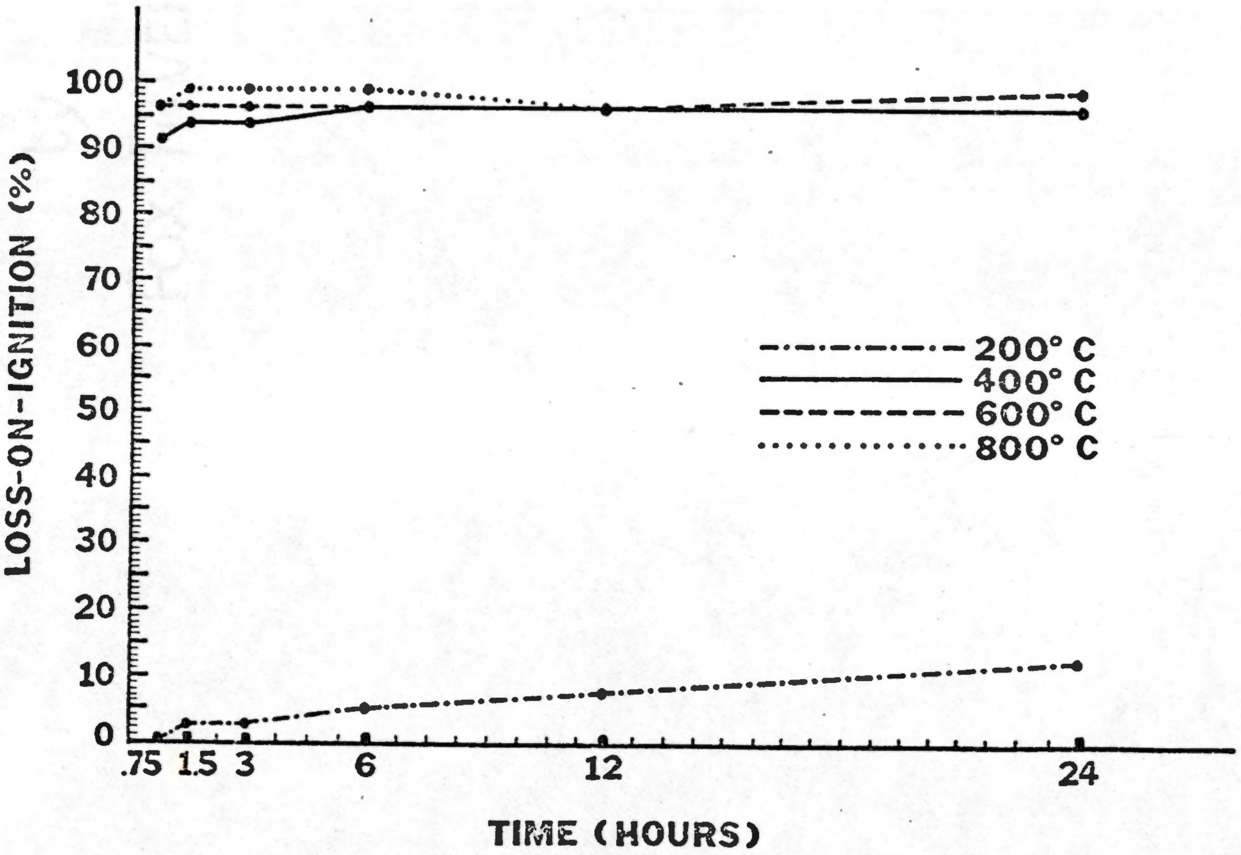

Figure 7. Loss-on-ignition of soybean stalk when ignited at different temperatures and times.

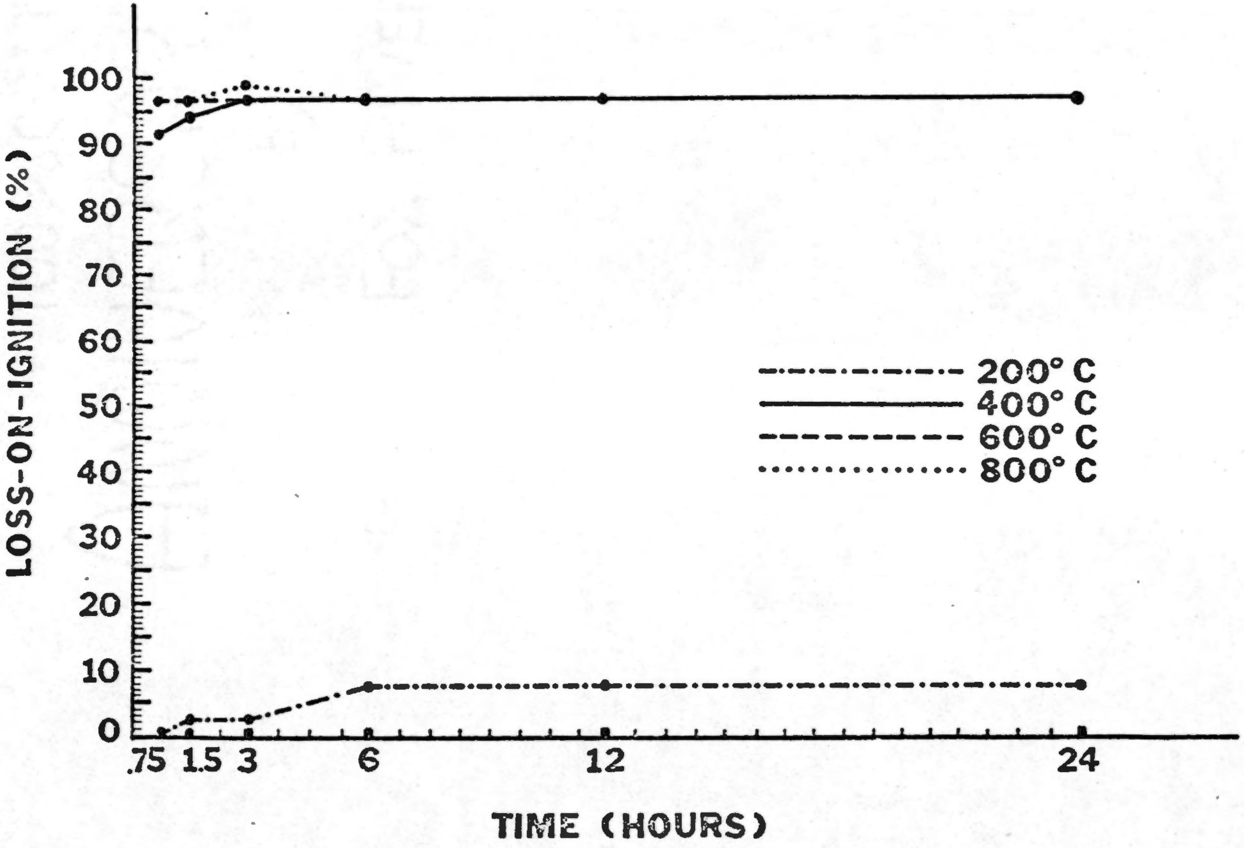

Figure 8. Loss-on-ignition of cotton stalk when ignited at different temperatures and times.

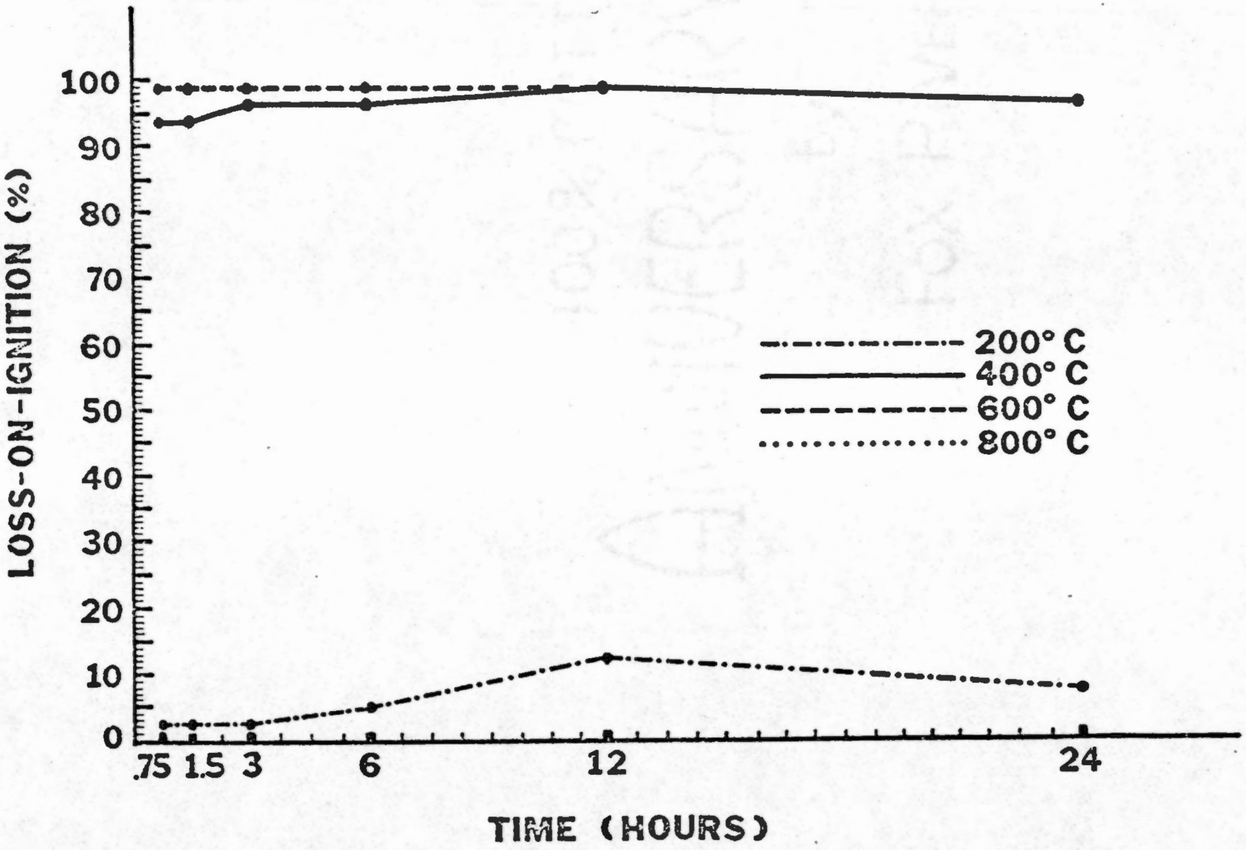

Figure 9. Loss-on-ignition of sphagnum peat when ignited at different temperatures and times.

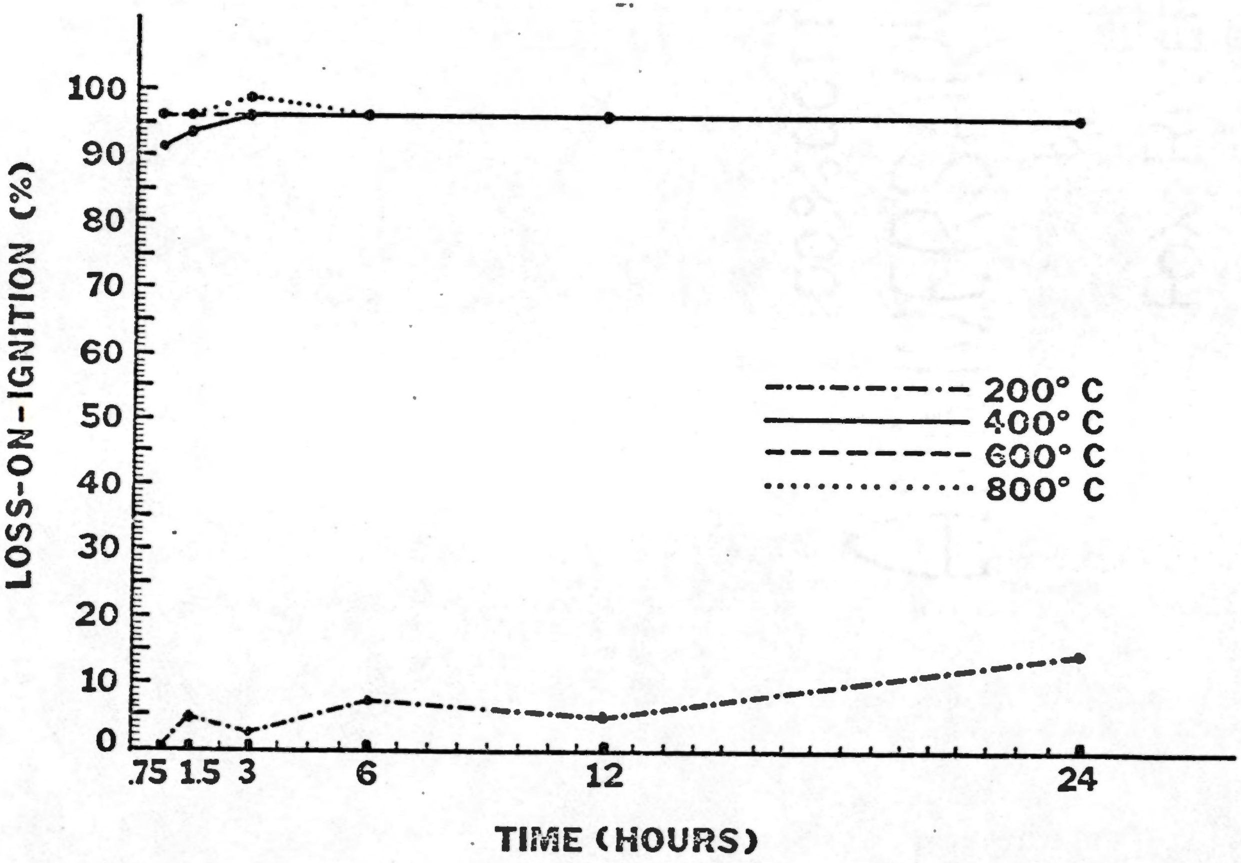

Figure 10. Loss-on-ignition of corn stalk when ignited at different temperatures and times.

increases which were variable and attributed to experimental error. The time period of heating became less important as the temperature was increased above 200°C. When these materials were ignited at 400°C, further weight losses with increased time were relatively small. There were increases in weight loss at short time periods but the losses showed a tendency to level off around a duration of 6 hours. Time of ignition had little effect on loss at 600 and 800°C. The loss-on-ignitions at these temperatures were nearly equal at all time durations. There were some small differences in these levels but they were values attributed to experimental error.

Mean separation tests for significance are not considered applicable to continuous data (13). In order to set a standard for efficiency of ignition, a value of 98 percent of maximum ignition was considered acceptable in this study. Thus, the ideal time period and temperature of ignition are considered to be the minimum values which will give 98 percent of maximum ignition. First priority is given to establishing the lowest possible temperature of ignition since many researchers have shown that errors due to weight loss of inorganic substances increase with increases in ignition temperature (6, 15, 24, 25). The minimum ignition temperature which gave acceptable ignition efficiency for each of these materials was 400°C (Tables 4 and 5, pages 40 and 41). The minimum time period giving acceptable efficiency varied slightly between these materials. Corn stalk and oak sawdust needed 3.0 hours at 400°C for acceptable ignition while cotton stalk, soybean stalk, and sphagnum peat required 6.0 hours at 400°C. However, the 6 hour duration is much shorter than the 16 hours recommended by Ball (6) and Keeling (24), the 24 hours recommended by Davies (15), or the 30 hours recommended by Kerr (26). Mitchell's (32) results were similar to those of this study. He recommended an 8 hour duration at 350 to 400°C. All the researchers listed above recommended ignition temperature similar to the 400°C found to be acceptable for these organic materials.

Michigan peat showed responses to changes in ignition temperature which were slightly different from the other organic materials. Maximum ignition loss was 88.90 percent (Table 5, page 41). This lower ignition loss might be expected since Michigan peat is known to contain a considerable soil fraction which would resist destruction by temperatures used in this study. Like the preceding organic materials, Michigan peat showed little weight loss when ignited at 200°C (Figure 11). Ignition losses at this temperature varied from 2.69 percent for 1.5 hours to 12.20 percent for 24 hours (Table 5). When the temperature of ignition was raised to 400°C the weight loss increased dramatically to values ranging from 74.63 to 86.60 percent. Further increases in ignition temperature to 600°C and then

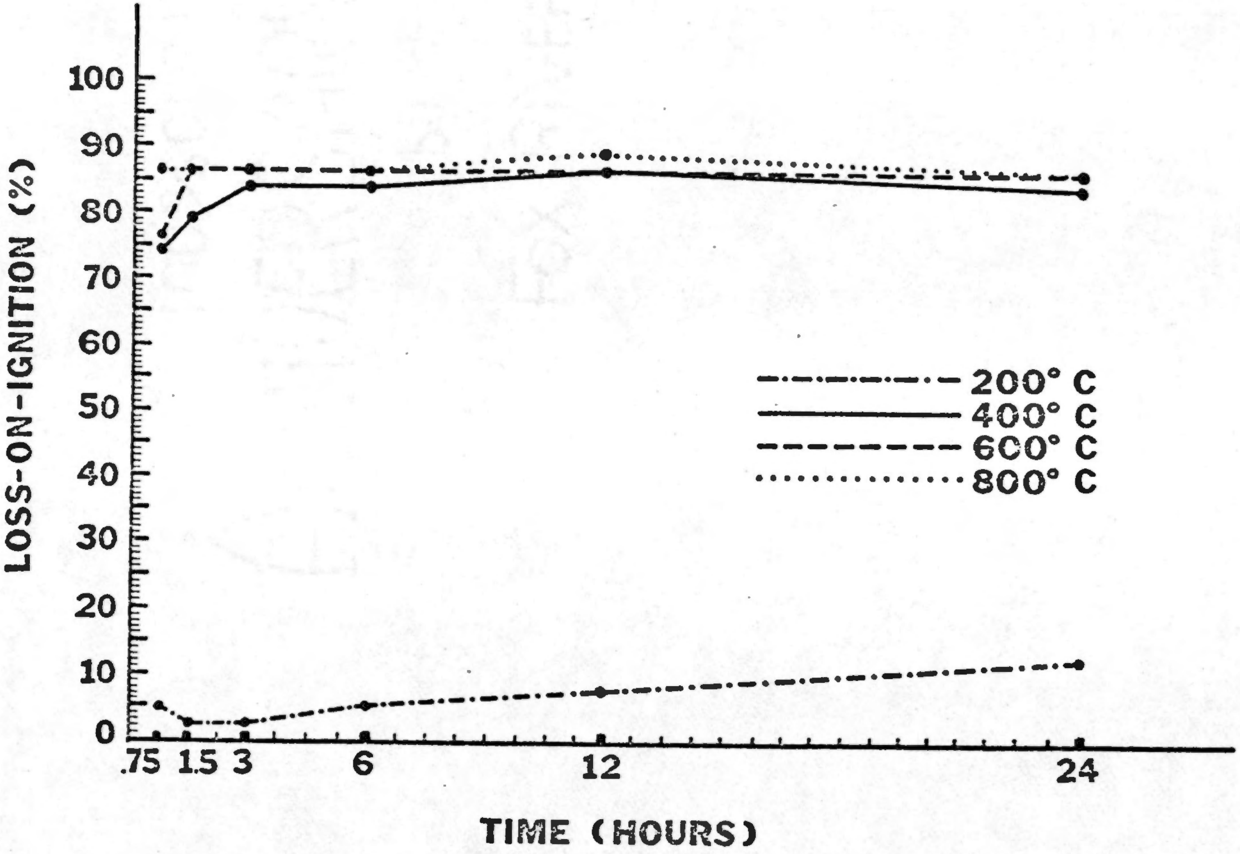

Figure 11. Loss-on-ignition of Michigan peat when ignited at different temperatures and times.

to 800°C resulted in very little additional loss. Losses from mineral fractions are known to be greatest at these very high temperatures. The additional losses of Michigan peat at the very high temperatures may be attributed to weight loss of the mineral portion. When the temperature was raised from 200 to 300°C for 1.5 hours (Figure 5, page 43) a very large increase in ignition loss was sustained. With a temperature from 300 to 400°C there was little difference in the loss. This differs considerably from the response of the previously discussed organic materials which showed large weight loss increases when the temperature was raised from 300 to 400°C. Michigan peat showed additional losses as the temperature was raised from 400 to 500°C and from 500 to 600°C. Little additional loss resulted from further temperature increases.

Effects of the time of ignition on ignition loss were similar to the first five organic materials discussed (Figure 11). When temperature was 200°C, a relatively linear increase in weight loss was observed as the time of heating was increased. At 400°C there was a large rise in weight loss when the duration was increased from 0.75 to 1.5 hours and 1.5 to 3.0 hours. Further increases in time resulted only in slight increases in weight loss. At 600°C there was a sharp increase in weight loss when the duration was increased from 0.75 to 1.5 hours. Further increases in duration resulted in little additional loss. Very little benefit was realized by duration increases at 800°C. Weight losses were similar at all durations.

The minimum temperature and time period for acceptable ignition of Michigan peat was 600°C for 24 hours (Table 5, page 41). This is a much higher temperature, a longer time period, and lower percent maximum weight loss than that which could be expected for the previous five organic materials. This discrepancy may be a result of the presence of relatively large amounts of mineral constituents.

Pine bark contained a surprisingly small organic fraction which was destroyed by the temperatures studied. Maximum weight loss was 69.38 percent (Table 5) and losses by time were highly variable suggesting the presence of considerable amounts of combustion resistant contaminants. Like the other organic materials, only small weight losses were observed at 200°C with values ranging from 1.60 to 9.13 percent (Figure 12 and Table 5). Pine bark also reacted similarly to the organic materials by showing a large increase in weight losses when the temperature was raised to 400°C. Values at 400°C varied from 49.94 to 64.30 percent. Weight losses at 100°C increments for a duration of 1.5 hours (Figure 5, page 43) showed pine bark having a trend similar to Michigan peat but with much lower corresponding temperature loss percentages. Pine bark showed a sharp increase in weight

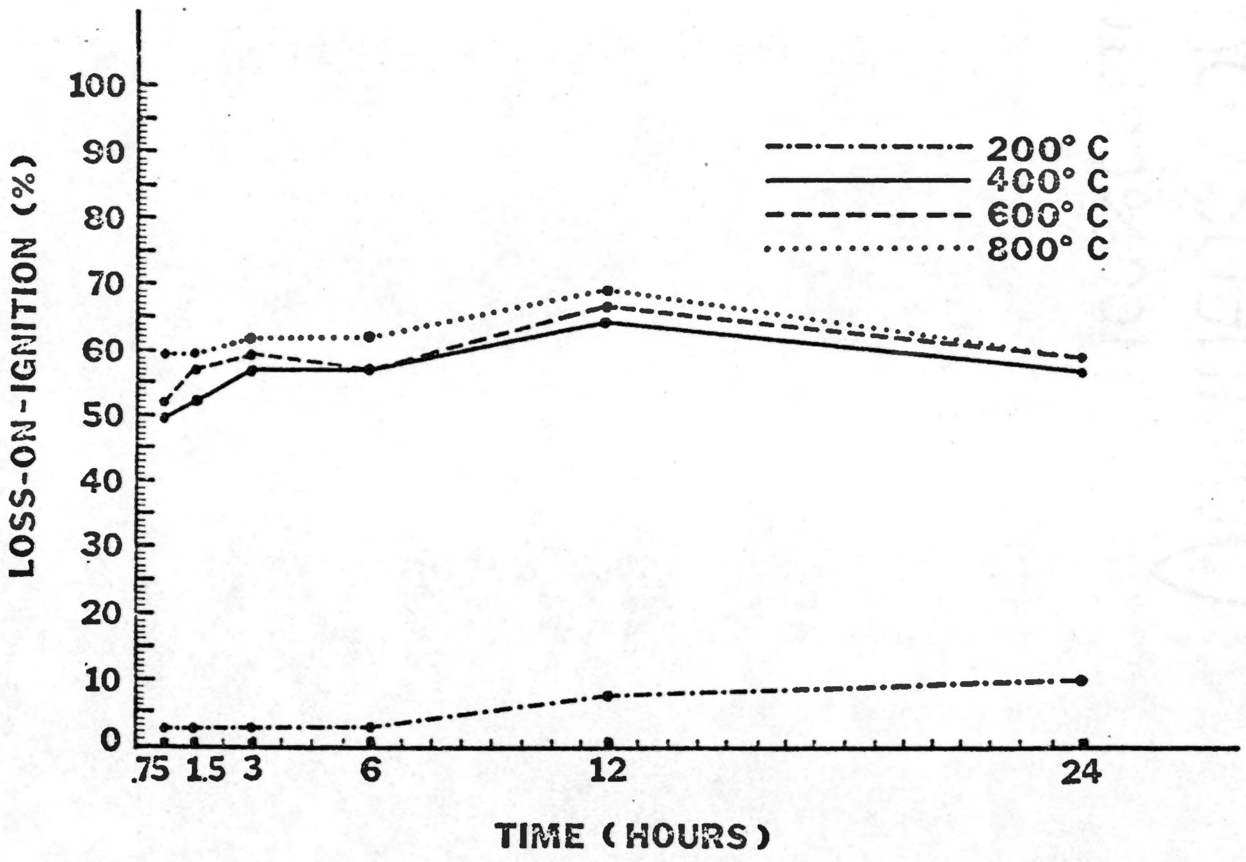

Figure 12. Loss-on-ignition of pine bark when ignited at different temperatures and times.

loss when the temperature was raised from 200 to 300°C. Like Michigan peat there was little increase when the temperature was raised above 300°C.

Sewage sludge had the lowest maximum weight loss of all the organic materials tested. The highest loss observed was 48.02 percent at 800°C (Table 5, page 41). The weight loss trends (Figure 13) of sewage sludge resembled those of the sands more than the other organic materials. Little loss was observed when the temperature was 200°C. The values ranged from 0.70 to 6.68 percent. When the temperature was raised to 400°C there was a considerable increase in the weight loss with a maximum weight loss of 33.40 percent. When the temperature was raised to 600°C only a slight increase in weight loss was realized with a maximum loss of 39.41 percent.

Sewage sludge weight losses at 100°C increments for 1.5 hours (Figure 5, page 43) showed the lowest overall corresponding loss percentages of the eight organic materials studied. Loss-on-ignition percentages followed more of a sigmoid type curve response gradually increasing with temperature.

Most of the previously discussed organic materials sustained close to maximum weight loss at 400°C. The sewage sludge studied contained a very large percentage, at least 51.98 percent, of combustion resistant unknown fractions, even at 800°C.

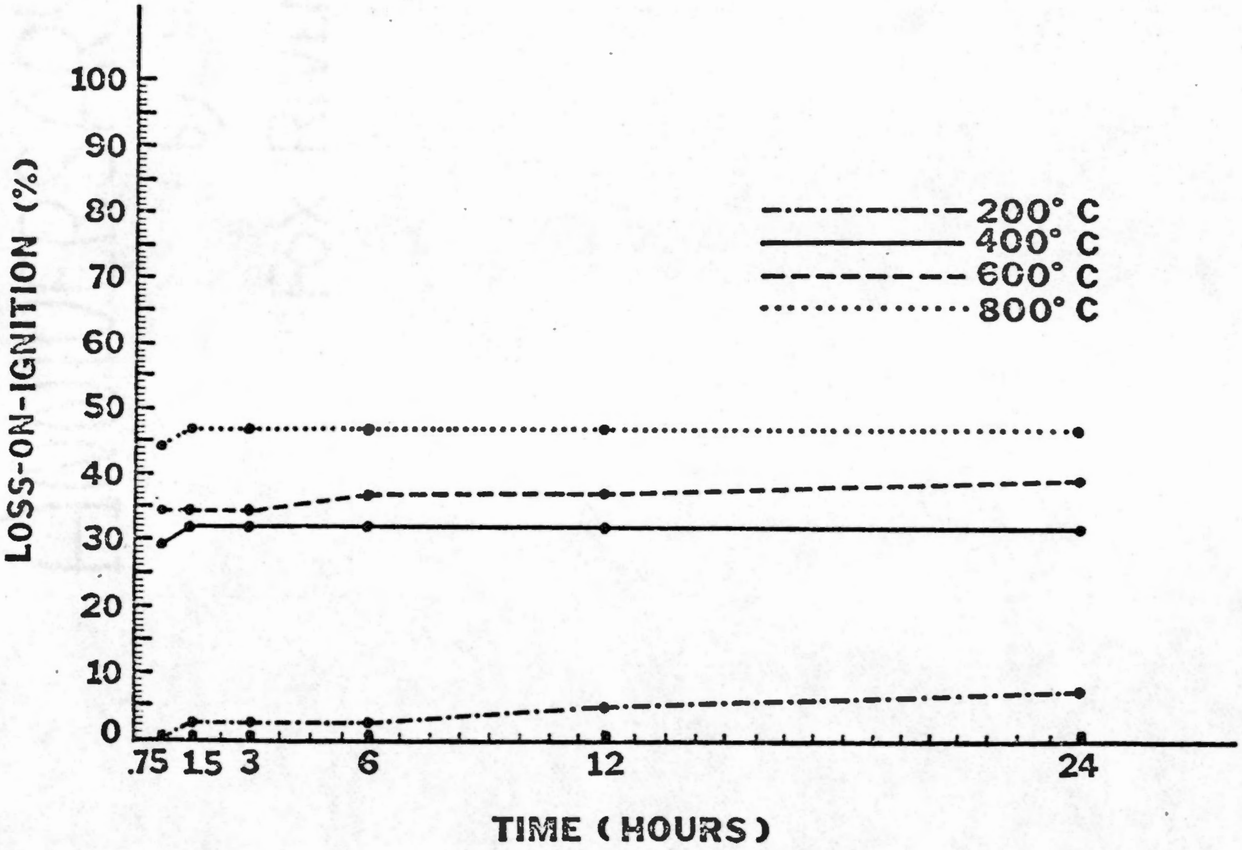

Figure 13. Loss-on-ignition of sewage sludge when ignited at different temperatures and times.

The minimum temperature and time period which gave at least 98 percent of maximum combustion fractions for sewage sludge was 800°C for 3.0 hours (Table 5, page 41). This is a much higher temperature than that required to achieve acceptable efficiency with the other organic materials studied.

Analysis of variance showed that time and temperature effects were significant for all organic materials at the 5 percent level of probability. As with the sands the magnitudes of the temperature effects for the organic materials were many times larger than those of the time effects. This would indicate that in all cases temperature was responsible for a very large portion of the total variation while the time duration of ignition was responsible for only a small portion.

III. Comparison of Methods

Combustible or digestible fractions of each sand and organic material were measured by three different methods of determination. Methods compared were the loss-on-ignition, Walkley-Black, and hydrogen peroxide. Loss-on-ignition was performed at 400°C for 6 hours.

Sands

There was no significant difference between the destructible fractions of brown sand measured by the loss-on-ignition and hydrogen peroxide methods (Table 6). The Walkley-Black method indicated a destructible fraction significantly lower than that measured by the other two methods. The destructible fraction of yellow sand was significantly higher when measured by the hydrogen peroxide method than when measured by the loss-on-ignition method (Table 6). The Walkley-Black method indicated a significantly lower fraction than that measured by either of the other two methods. Tests on white sand showed the hydrogen peroxide method again measured a significantly higher level than either of the other two methods (Table 6). There was no significant difference, however, between the levels measured by the loss-on-ignition and Walkley-Black methods.

Results would seem to indicate that the hydrogen peroxide method gave the most efficient measure of organic matter in these sands. This does not concur with results of other researchers who have found this method to be relatively inefficient (1, 4, 29, 47). It is possible that the high values could be artificial due to experimental error. The nature of this method makes this type of error likely. Results by the Walkley-Black method were much lower in all cases with loss-on-ignition results giving values between the other two. This would agree with other researchers who have found the loss-on-ignition method to be relatively efficient

Table 6. Combustible or digestible content of three sands as determined by three methods.

Sand Material	Combustible or Digestible Fraction (% by Wt.)[1]		
	Loss-on-Ignition	Walkley-Black	Hydrogen Peroxide
Brown Sand[2]	0.44 a	0.04 b	0.54 a
Yellow Sand	0.34 b	0.03 c	0.68 a
White Sand	0.13 b	0.03 b	0.38 a

[1] Loss-on-ignition was performed at 400°C for 6 hours.

[2] Means within rows followed by the same letter are not significantly different at the 0.05 level of probability according to Duncan's Multiple Range Test.

(6, 15, 24) while the Walkley-Black method is known to measure only that organic matter which is readily oxidizable (3, 12, 50).

Organic Materials

Corn stalk, cotton stalk, oak sawdust, and soybean stalk responded similarly to the three organic matter determination methods. The ignition loss of each of these materials was very high ranging from 96.88 to 97.57 percent (Table 7). In each case ignition loss was significantly higher than results by the Walkley-Black method which ranged from 75.68 to 77.10 percent. The digestible fraction measured by the hydrogen peroxide method was significantly lower than that measured by the other two methods. Hydrogen peroxide results were relatively inconsistent varying from 25.00 to 47.11 percent. These four organic materials were also similar in that they were all plant materials. Bremner and Jenkinson (8) reported that the Walkley-Black method gave near 100 percent measurement on plant materials. These results do not substantiate their findings.

Sphagnum peat gave the highest values of destructible fraction with the loss-on-ignition method (Table 7). The loss-on-ignition mean was 97.60 which was significantly higher than the hydrogen peroxide value of 85.50. Sphagnum peat differed from the previous four organic materials in

Table 7. Combustible or digestible content of eight organic materials as determined by three methods.

Organic Material	Combustible or Digestible Fraction (% by Wt.)[1]		
	Loss-on-Ignition	Walkley-Black	Hydrogen Peroxide
Sphagnum Peat[2]	97.6 a	74.0 c	85.5 b
Soybean Stalk	97.6 a	76.7 b	25.0 c
Oak Sawdust	97.5 a	75.7 b	47.1 c
Cotton Stalk	97.2 a	76.8 b	26.2 c
Corn Stalk	96.9 a	77.1 b	38.1 c
Michigan Peat	85.6 b	72.7 c	89.6 a
Pine Bark	56.8 b	45.8 c	66.2 a
Sewage Sludge	32.7 a	26.7 c	32.0 b

[1] Loss-on-ignition was performed at 400°C for 6 hours.

[2] Means within rows followed by the same letter are not significantly different at the 0.05 level of probability according to Duncan's Multiple Range Test.

that the Walkley-Black values were the lowest, with a digestible fraction of 74.02 percent.

Responses of Michigan peat and pine bark were different from the other organic materials with some similarities to each other (Table 7). Hydrogen peroxide values were significantly higher than those of the other two methods. Values measured by loss-on-ignition were significantly greater than those measured by the Walkley-Black method. Michigan peat and pine bark are both known to contain considerable inorganic contaminants. These contaminants seemed to result in lower combustible or digestible fraction percentages for pine bark than Michigan peat.

Sewage sludge gave very low combustible or digestible fraction values which were much lower than the other organic materials tested (Table 7). Loss-on-ignition values were the highest at 32.73 percent and significantly higher than the hydrogen peroxide values of 31.96 percent. The Walkley-Black values were very low at 26.68 percent. While the differences between the methods were significant, there was less variation than with any of the other organic materials.

Relationships Between Methods

Regression analysis indicate that a near linear relationship exists between combustion values by the loss-on-ignition method (800°C for 6 hours) and the digestion values by the Walkley-Black method for the eight organic materials studied (Figure 14). The regression response began with low values and evolved into a slight sigmoid curve of increasing values. The percent organic matter by Walkley-Black intercept was very near zero indicating little error at that point. At 100 percent by loss-on-ignition the regression plot indicates about 78 percent by the Walkley-Black method (Figure 14). This is very close to the average of 76 percent that Walkley and Black (50) reported that their method would recover. The very good relationship between these two methods would seem to make the choice between them one of personal preference. If the Walkley-Black method is used, however, an appropriate correction factor must be employed to allow for the incomplete organic matter recovery.

Hydrogen peroxide and loss-on-ignition methods showed a nonlinear relationship (Figure 15). This analysis was run only on loss-on-ignition values below 90 percent due to the wide range of values above that level. The percent organic matter by hydrogen peroxide intercept was near zero and the curve formed a sigmoid pattern of increasing values. There seemed to be a good relationship between the two methods until loss-on-ignition values were above 90 percent. When loss-on-ignition values were above 90 percent there was considerable inconsistency between the results by the hydrogen peroxide method. This would seem to agree with the results of Robinson (39) who found that some constituents in soil

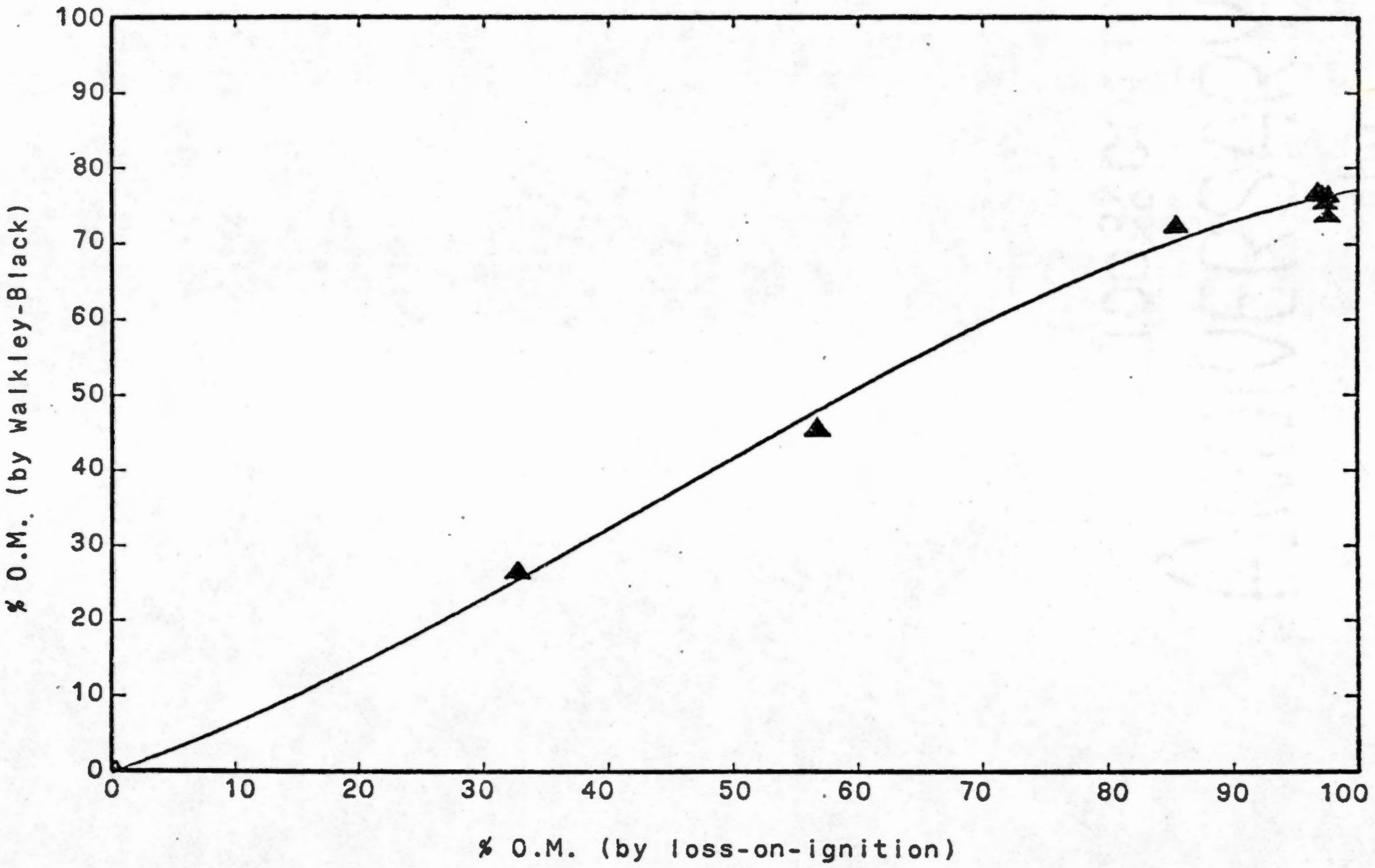

Figure 14. Regression of combustible and digestible fractions of eight organic materials by the Walkley-Black method compared with values by the loss-on-ignition method.

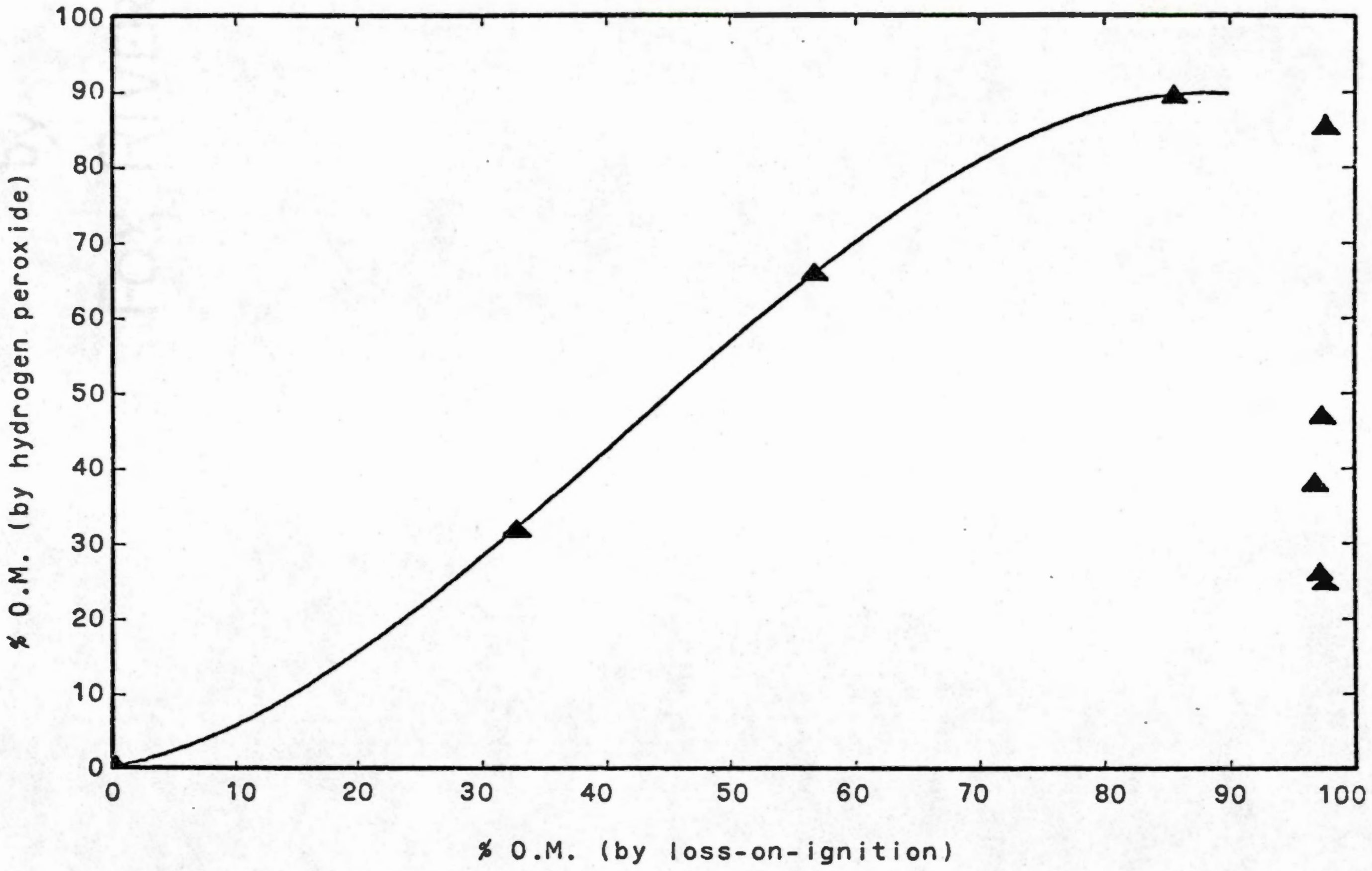

Figure 15. Regression of combustible and digestible fractions of eight organic materials by the hydrogen peroxide method compared with values by the loss-on-ignition method.

seemed to catalyze the destruction of organic matter by hydrogen peroxide. The organic materials which seemed to give reasonably good results with the hydrogen peroxide method were Michigan peat, pine bark, sphagnum peat, and sewage sludge. These materials appear to contain some catalyst for the reaction. Corn stalk, cotton stalk, oak sawdust, and soybean stalk are all plant materials appearing not to contain a catalyst. Preliminary studies in these investigations seemed to indicate that mixing of the plant materials with sand did not greatly improve the ability to analyze for the organic materials. Indications are that the hydrogen peroxide method is not a reliable procedure to use with many of the sand-organic matter soil mixes used in the turfgrass industry today.

CHAPTER 5

SUMMARY

The purpose of this study was to determine the applicability of three methods of organic matter determination on the components of high organic matter-sand mixes used in the turfgrass industry. An additional objective was to determine the lowest temperature and shortest time period for optimum results with the loss-on-ignition method.

I. Loss-on-Ignition Method

Weight losses of three sands and eight organic materials were measured at various temperatures and time periods. White sand was found to contain the smallest combustible fraction while brown and yellow sand contained considerably more. All sands showed an increase in weight loss with increasing temperature with the sharpest weight losses occurring as the temperature was raised above 400°C. A portion of loss above 400°C may reflect error due to weight loss from crystalline mineral contaminants in the sands. There was a general increase in weight loss as time period of heating was increased from 0.75 to 24 hours. These increases were much smaller in magnitude than increases resulting from temperature effects. Results indicated that with the loss-on-ignition method temperature control is most important. A temperature of 400°C for a time period of 6 hours was needed for acceptable ignition of the sands. At this temperature and time period destruction of organic materials was near maximum while destruction of mineral contaminants was minimal.

Loss-on-ignition showed close similarities between the organic materials corn stalk, cotton stalk, oak sawdust, soybean stalk, and sphagnum peat. All showed small losses at 200°C, large losses at 300°C, and another considerable increase at 400°C. Above 400°C there was little additional loss thus indicating 400°C to be the lowest temperature giving reliable results for these materials. Increases in the time period of heating resulted in general increases in ignition losses but the losses tended to level off at 6 hours. These results generally indicate little justification in continuing the ignition time beyond 6 hours.

Michigan peat contained considerable amounts of noncombustible materials resulting in lower maximum weight losses than the preceding group of organic materials. Michigan peat showed very large losses up to 300°C, slight losses from 300 to 600°C, then leveled off above 600°C. Thus, a temperature of 600°C appeared necessary to achieve complete loss of the combustible fraction. Michigan peat required a longer time period for complete combustion than the previous group also. The time period for acceptable ignition was 24 hours at 600°C.

Pine bark contained a large noncombustible fraction, about 30 percent by weight, thus giving lower combustion loss values than Michigan peat. The results indicated a temperature of 800°C was needed to give an acceptable level of of ignition. Results from increases in the time period of heating were variable but showed a maximum loss-on-ignition at 800°C to occur with a time period of 12 hours.

Sewage sludge showed the highest noncombustible fraction and lowest maximum ignition loss of all the organic materials. Like pine bark a temperature of 800°C appeared necessary to give an acceptable level of ignition. However, a time period of only 3 hours was needed to give acceptable weight losses at 800°C.

The organic materials which contained very small amounts of noncombustible contaminants all sustained acceptable ignition at 400°C for 6 hours. These materials were corn stalk, cotton stalk, soybean stalk, oak sawdust, and sphagnum peat. The other three organic materials contained considerable quantities of noncombustible contaminants and required higher temperatures and/or longer time periods to achieve acceptable ignition losses, except for the shorter time period for sewage sludge. It would seem that if 400°C for 6 hours was sufficient to destroy the combustible fraction of the organic materials in the first group that the same treatment would have the same results with the other organic materials tested. A higher temperature and longer time period was necessary thus indicating the presence of materials which are not organic. It is known that Michigan peat, pine bark, and sewage sludge contain considerable and variable amounts of inorganic materials. Therefore, possibly the organic components of these test materials were ignited to an acceptable level by 400°C for 6 hours and the higher temperatures and longer time periods were destroying inorganic fractions. If this is true then 400°C for 6 hours would be the optimum temperature and time period for ignition for all the organic materials tested.

II. Hydrogen Peroxide Method

The hydrogen peroxide method produced higher values for the sands than did either the Walkley-Black or loss-on-ignition method. Indications are that these values are artificially high due to the nature of this method, thus a correction factor may be needed.

Results of the hydrogen peroxide method on organic materials were highly variable. The destructible fractions measured by this method were the highest of all the methods for Michigan peat and pine bark and were the lowest for corn stalk, cotton stalk, oak sawdust and soybean stalk. Values for sphagnum peat and sewage sludge fell between those by the other two methods.

A poor relationship existed between the hydrogen peroxide and loss-on-ignition methods. This poor relationship was a result of the highly inconsistent values displayed by the hydrogen peroxide method on the organic materials which appeared to contain a very small noncombustible fraction when ignited. Due to these inconsistencies the hydrogen peroxide method is deemed unacceptable for many high organic matter-sand mixes and is not recommended for use in turfgrass research.

III. Walkley-Black Method

The Walkley-Black method produced much lower values for the destructible fraction in the sands than did either of the other two methods. This might be expected since this method is known to measure only the easily oxidizable fractions of organic materials and has little effect on mineral constituents.

Walkley-Black values for the organic materials were lower than loss-on-ignition values in all cases and lower than hydrogen peroxide values for Michigan peat, pine bark, sewage sludge, and sphagnum peat. The lower values tended to correspond with those materials containing considerable mineral contaminants.

A good relationship generally existed between the Walkley-Black and loss-on-ignition methods. The relationship was nearly linear. This is consistent with reports by other researchers (2, 3, 15, 50) which show the Walkley-Black method to measure only the easily digestible fraction. However, a correction factor would be necessary to achieve consistent results. The Walkley-Black method is deemed acceptable for high organic matter-sand mixes containing predominantly easily digestable organic fractions if a reliable correction factor can be determined.

CHAPTER 6

CONCLUSIONS

The loss-on-ignition method was the most reliable of the three methods studied for both sand and organic materials. Loss-on-ignition was more meaningful than the Walkley-Black method and much more consistent than the hydrogen peroxide method.

Ignition of sands was most reliable at 400°C for 6 hours. Further investigations are needed to clearly identify crystalline mineral materials in sands and the specific temperatures of their weight loss and eventual destruction in order to reduce potential errors.

A temperature of 400°C for 6 hours gave acceptable results for corn stalk, cotton stalk, oak sawdust, soybean stalk, and sphagnum peat. However, the other three organic materials indicated a presence of considerable quantities of contaminants consisting of crystalline minerals, combustion resistant organic fractions, and other unknowns. Consequently higher temperatures and/or longer time periods were needed to achieve complete combustion. Temperatures and time periods for complete combustion of Mighigan peat was 600°C for 24 hours, 800°C for 12 hours for pine bark, and 800°C for 3 hours for sewage sludge. However, it is theorized that 400°C for 6 hours should be sufficient to destroy the combustible fractions of organic matter in the latter three materials. The higher temperatures appeared to be a result of an unknown quantity of destructible contaminants that could not be easily recognized by the general procedures employed in these investigations. Additional research is needed to accurately define the specific temperature and time needed to destroy only the combustible fractions of all the organic materials studied in these investigations.

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VITA

David Shelby Cochran was born in Jacksonville, Florida, on December 13, 1952. He attended elementary school at Alice Bell School in Knoxville, Tennessee, and graduated from Holston High School in 1970. He entered The University of Tennessee in the summer of 1970 and received a Bachelor of Science degree with a major in Ornamental Horticulture and Landscape Design in March 1978.

In March 1978, he entered graduate school at The University of Tennessee majoring in Ornamental Horticulture and Landscape Design. He was granted the Master of Science degree from The University of Tennessee in March 1980 with a major in Ornamental Horticulture and Landscape Design. While working toward his degree, he was employed by The University of Tennessee Agricultural Experiment Station as a Graduate Research Assistant in Ornamental Horticulture and Landscape Design.