Technical Memorandum

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Final Report

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c/o John Shoucair

Geotechnical Materials Engineer

FDOT State Materials Office

Submitted by:

Dr. Elise Morrison (elise.morrison@essie.ufl.edu) (Principal Investigator)

Dr. Kyle A. Riding (Co-Principal Investigator)

Dr. Christopher C. Ferraro (Co-Principal Investigator)

Engineering School of Sustainable Infrastructure and Environment

University of Florida
Gainesville, Florida 32611

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Department of Civil Engineering

Engineering School of Sustainable Infrastructure and Environment

College of Engineering

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Prepared in cooperation with the State of Florida Department of Transportation and the U.S. Department of Transportation.

SI (MODERN METRIC) CONVERSION FACTORS (FROM FHWA)

Symbol	When You Know	Multiply By	To Find	Symbol
Length				
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
Area				
in²	square inches	645.2	square millimeters	mm²
ft²	square feet	0.093	square meters	m²
yd²	square yard	0.836	square meters	m²
mi²	square miles	2.59	square kilometers	km²
Volume				
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft³	cubic feet	0.028	cubic meters	m³
yd³	cubic yards	0.765	cubic meters	m³
NOTE: volumes greater than 1000 L shall be shown in m³				
Mass				
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
Temperature (exact degrees)				
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C
Illumination				
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m²	cd/m²
Force and Pressure or Stress				
lbf	pound-force	4.45	newtons	N

lbf/in²	pound-force per square inch	6.89	kilopascals	kPa

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16. Abstract

Fine aggregates used for concrete can sometimes contain organic matter that can inhibit the cement hydration reactions and reduce strength. AASHTO T 21 and AASHTO T 71 have been developed as screening tests for fine aggregate organic matter and quality. The objective of this research project is to determine whether a modified Walkley Black test or Elemental Analysis of carbon test can be used as a substitute test for the AASHTO T 21 or AASHTO T 71 tests. Organic content for 18 fine aggregate samples from Florida and Georgia were measured using the Modified Walkley Black method and Elemental analysis via combustion and compared to the results of AASHTO T 21 and AASHTO T 71. A good correlation was found between the Modified Walkley Black method and Elemental analysis via combustion and AASHTO T 21, however none of the tests correlated well with AASHTO T 71. Isothermal calorimetry performed on mortar samples did not show that the fine aggregates caused any cement hydration retardation or interference with the cement hydration reaction. Any mortar strength loss must be due to other factors that should be investigated in the future.

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EXECUTIVE SUMMARY

Background

Portland cement concrete is composed of at least four main ingredients: portland cement, water, coarse aggregate (rocks), and fine aggregate (sand) [1]. The strength and performance of the overall concrete is dependent on the quality of each ingredient and any interactions that may occur between them. The fine aggregates may include some undesirable material besides aggregates, such as clay particles and organic material. Some organic materials can be undesirable, as they can dissolve and inhibit the cement hydration reactions and cause an increase in setting time or loss in strength [2], [3],[4]. However, other types of organic material, like activated carbon, can absorb water and chemical admixtures, but do not necessarily decrease strength [5]. Thus, quantifying the amount and identifying the type of organic material in fine aggregate could provide useful information about whether cement strength or setting time may be adversely affected by fine aggregate (sand). Currently, the Florida Department of Transportation (FDOT) uses the American Association of State Highway and Transportation Officials (AASHTO) T 21 to screen fine aggregates for organic content, and if they are found to have excessive organic material, uses AASHTO T 71 to determine if the fine aggregate negatively impacts the strength.

Research Objectives

The objective of this research project is to determine whether a modified Walkley Black test or elemental analysis of carbon can be used as a substitute test for the AASHTO T 21 or AASHTO T 71 tests.

Main Findings

Project findings can be summarized as follows:

- The Modified Walkley Black method (MWB) and Elemental analysis (EA) via combustion were both identified as tests that could be performed quickly (< 5 days) and affordably (< \$100/test), thereby meeting the criteria for speed and affordability.
- The MWB method and EA method were in general agreement regarding total carbon content, with the exception of mine 05045. It was also noted that there was temporal variability in the carbon content of each mine, based on the T 21 color tests and MWB results, highlighting the need for continued monitoring, rather than one timepoint.
- While it was found that tests could meet the cost and time requirements, there did not appear to be a relationship between the % total carbon of a sand sample (either via the MWB or EA method), with concrete strength, as measured by the T 71 mortar cube test (either 7-day or 28-day).
- The lack of relationship between the total carbon content and the T 71 mortar cube test suggest that either the type of carbon or other interfering compounds may reduce concrete strength, rather than total carbon. It was found that there was a positive relationship between $\delta^{13}C$ values and T 71 mortar cube test results, which may indicate that the source/type of carbon influences early cement hydration processes.

- Based on the results of these tests, it is recommended that either the MWB or EA can reliably determine the total carbon in a sand sample. However, neither test was related to T 71 test results, indicating that these tests are not suitable for replacing AASHTO T 71.

Recommendations

Based upon the findings from this study, the following recommendations are made:

- Either the elemental analysis of carbon or the modified Walkley Black test can be adopted to measure carbon content in fine aggregate in lieu of the AASHTO T 21 test.

Further Research

The following areas of future research needs have been identified:

- Investigate the mechanism in which Florida fine aggregate organic material impacts the mortar strength in AASHTO T 71
- There was a slightly negative relationship between phosphorus content and the T 71 mortar cube test results (for both day 7 and day 28), suggesting that phosphorus may interfere with concrete strength. However, this relationship was weak, and further investigation is needed.
- Additional analyses need to be conducted to investigate other mechanisms that might interfere with concrete strength.

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1. INTRODUCTION

Portland cement concrete is composed of at least four main ingredients: portland cement, water, coarse aggregate (rocks), and fine aggregate (sand) [1]. The strength and performance of the overall concrete is dependent on the quality of each ingredient and any interactions that may occur between them. Fine aggregate contains all particles that are smaller than the No. 4 sieve (0.187in). These smaller particles may include some undesirable material besides aggregates, such as clay particles and organic material. Clay particles are undesirable because they are expansive, absorb water and chemical admixtures and inhibit bonds between the aggregates and the cement paste [2]. Some organic materials can also be undesirable, as they can dissolve and inhibit the cement hydration reactions, causing a loss in strength [3], or an increase in setting time [2],[4]. However, other types of organic material, like activated carbon, can absorb water and chemical admixtures, but do not necessarily decrease strength [5]. Thus, quantifying the amount and identifying the type of organic material in fine aggregate could provide useful information about whether cement strength or setting time may be adversely affected by fine aggregate (sand).

1.1. Mechanisms by which organic matter can affect cement hydration

Soil organic matter is a complex mixture of organic (carbon-containing) substances that is largely derived from the decomposition of biological material (vegetation, bacteria, etc.). In general, organic matter is comprised of approximately 50% carbon by weight [6]. Traditionally, organic matter in soils has been divided into humic acids, fulvic acids, and humin (humic substances), and non-humic substances, which are operationally defined based on their solubility. Humic acids are soluble above a pH of 2 and a molecular weight > 10,000 Da, fulvic acids are soluble at any pH and are approximately 500 Da, and humin is not soluble across the full pH range. However, humic substances are highly variable in their chemical composition, can include carbon chains, rings, and active functional groups [7], and there is considerable scientific debate about the nature and molecular composition of these operationally defined substances [8], [5], [9]. Nonetheless, some acids found in soils and fine aggregates such as humic acid, acetic acid, or tannic acid, or sugars like sucrose are known to affect cement hydration, increase setting time and reduce strength [10], [11].

Cement is a powdery substance that can be mixed with sand, rock, and water to produce concrete. This mixture generates an exothermic reaction called hydration, where dissolution initially produces a large amount of heat but slows down until the cement hardening rate accelerates again [12]. Organic matter can affect cement hydration by one of four mechanisms: (1) adsorption onto cement particles blocking dissolution of the cement; (2) complexation with ions such as calcium; (3) precipitation onto cement particles; or (4) poisoning nucleation or growth of hydration products, or a combination of two or more of these mechanisms [13]. For example, sugars are thought to affect cement hydration reactions by adsorbing to Ca to prevent Calcium-Silicate-Hydrate (C-S-H) (the glue that binds together concrete) from forming [14]. Some organic admixtures can either increase or decrease the time of initial set of the cement depending on the dosage [8], [15]. The amount and type of organic matter in silica sand determines whether it will affect the cement reaction and be suitable for use in portland cement concrete.

Organic matter in soils can also act as retarding agents in cement setting and solidification [16]. In cements that were treated with organic acids that produced a pH less than 9 in the cement pore solution, almost no strength gain was seen [9]. However, not all organic material is equally effective, and cement setting is mainly affected by an 'active' fraction of organic compounds, mostly being glucose and nucleic acid, which adsorb calcium ions liberated during hydration [3]. For instance, sucrose and raffinose are the most effective retarders, whereas reducing sugars, glucose, maltose, lactose, and cellobiose are strong retarders [11]. Conversely, methyl glucoside and trehalose are non-retarders. Overall, the presence of sugars during the aqueous phase of hydrating cement increases the concentration of calcium, hydroxide, silicon, aluminum, and iron [17]. Furthermore, organic acids that produce a pH lower than 9 in the pore solution, when mixed with cement and soil, prevent the development of the cementing products because the pH is too low to allow secondary phase formation. Oils and hydrocarbons are also strong retarders of cement hydration but do not affect the final concrete strength [9].

1.2. Current FDOT Test Methods for the Determination of Organic Content

The current method used to measure organic content in fine aggregate is the American Association of State Highway and Transportation Officials (AASHTO) T 21 [18], which uses sodium hydroxide to react with the organics from the sand. The sand in the sodium hydroxide solution is allowed to settle for 24 hours, after which the color of the liquid is compared against standard colors on the Gardner Color Standard to rank the organic content. If the sample scores either a four or five, then further mortar testing is warranted. As specified by Florida Department of Transportation (FDOT) specification 902, AASHTO T 71 is used to determine if organic material in sand reduces the 28-day strength by more than 5%. This is conducted by measuring the mortar compressive strength of the sand as-received and comparing it to the mortar compressive strength of the sand washed with sodium hydroxide and rinse water to remove the organic material.

A Federal Highway Administration (FHWA) report on Florida fine aggregate showed there was a high level of organic matter as detected by AASHTO T 21 and attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR), but the sample passed AASHTO T 71 for mortar strength and could be used in concrete. Thus, a high level of organic matter detected in fine aggregate samples does not automatically mean that the material interferes with cement hydration, nor does it automatically disqualify it from use in concrete. Additionally, a study on soil-cement mixtures showed that some organic acids that caused a drop in 28-day unconfined shear strength also caused drops in the pore water pH and increases in sulfate content in the soil-cement systems. The same drop in pH and increase in sulfate content was not found however in samples that contained sucrose that also showed a decrease in strength. All of the compounds in that study that showed a decrease in strength also showed an increase in calcium content in pore solution measurements [9]. Although this study was performed with extremely high concentrations of added organic materials, it highlights the potential for a test method based on reactivity with portland cement that could replace both AASHTO T 21 and AASHTO T 71.

AASHTO T 21 does not have sufficient resolution of organic material quantity, nor does it identify the type of organics present to determine if the material organics have changed significantly since the last passed AASHTO T 71 test, requiring further expensive mortar testing. Even if a new test method to measure organic material in fine aggregates doesn't correlate with

strength in portland cement, it may be beneficial if it can determine if the quantity or type of organics has not changed from previous tests, eliminating the need for more extensive and expensive testing. It is also somewhat problematic that AASHTO T 71 has a higher coefficient of variation at 5.4% than the acceptable difference between washed and unwashed aggregate in FDOT 902 specifications, making it possible for bad material to be used, or good material to be rejected.

1.3. Alternate Test Methods for the Determination of Organic Content

Several test methods besides AASHTO T 21 have been developed by the soil science community to give quantitative measures of soil organic content. Generally, methods that measure organic matter (or carbon) content are based on either wet chemical oxidation (WCO) techniques that use chemical reagents to oxidize the carbon, or combustion methods that involve heating the sample in an oxygen-rich environment to convert organic carbon to carbon dioxide, which is subsequently analyzed. In addition to WCO and combustion methods, simple loss on ignition (LOI) is commonly used in soil science to calculate organic matter content based on the difference in mass between the soil sample heated to just above water boiling temperatures to dry the material and just above the temperature at which the organic matter decomposes. Here methods are reviewed that are commonly used to quantify organic matter, including organic carbon, to assess their suitability as tests for organic matter (or organic carbon) content in fine aggregate. Although there are a variety of methods utilized to measure total organic carbon, recent studies have found high correlation coefficients between the three most common methods: wet oxidation, loss on ignition, and elemental analyzer [19]. However, each of these methods has specific benefits and drawbacks, which must be considered for their application to evaluate organic matter in silica sand.

In general, the tests for determination of organic matter in soil samples can be classified into LOI, WCO methods, and dry combustion methods. The loss on ignition method is a simple, indirect measurement of organic matter, but it is prone to errors and is not as accurate as some of the other methods discussed. Most wet chemical oxidation methods, such as the modified Walkley-Black method (MWB) use potassium dichromate to oxidize about 50% of the carbon content in a sample and provide approximations of organic matter but can underestimate organic matter content. Dry combustion methods, such as Elemental Analysis (EA) via combustion have begun to replace the use of wet chemical oxidation methods in certain applications, since their measurements are rapid, automated, and allow for greater sample throughput. In a study that compared the reliability of all three methods (LOI, wet chemical oxidation, dry combustion), the dry combustion method had more accurate values with smaller uncertainty [19].

Methods that quantify the amount and identify the type of organic material in fine aggregate could provide useful information about whether cement strength or setting time may be adversely affected by sand and may help minimize the use of additional mortar testing. Here the AASHTO T 21 color test and T 71 mortar cube test results with the MWB and EA are compared to determine if either test may be a suitable replacement for either the T 21 color test and/or the T 71 mortar cube test. The selection of these tests was determined after a literature/industry review of methods (Task 2); a report summarizing recommended tests and meeting discussion (Task 3), and a Draft Work Plan specifying which mines would be tested (Task 4). Based on the recommended tests from Task 4, and on conversations between the University and the

Department, the following tests were run, with their respective labs in parentheses: T 71 Mortar Cube Test (Department); T 21 Color Test (University); MWB (University); and EA via combustion (University). Additional tests at the University of Florida were conducted to evaluate the concentration of other elements that may interfere with concrete setting, including zinc (Zn), boron (B), and phosphorus (P). Isothermal calorimetry was also conducted at the University to evaluate how each sand sample influenced cement hydration.

This report summarizes the project findings, including the results of chemistry, T 21 and T 71 tests, and analysis. It was found that the T 21 color test was in agreement with the chemistry tests, particularly the MWB method. However, no relationship between the T 21 color test and the T 71 mortar cube tests was found, either for day 7 or day 28 strength. Similarly, a strong relationship was not found between the chemistry tests and the T 71 mortar cube tests. The isothermal calorimetry results did not indicate significant interference of the organic material in the sand with the cement hydration.

2. FINE AGGREGATE SAMPLES

Samples from 12 facilities (one sample/facility) were retrieved from the State Materials Office in early January 2022. Samples from six facilities were retrieved from the State Materials Office in mid-March 2022. Samples are summarized in Table 1. Facilities were selected to provide samples representative of a wide range of T 21 color scores, based on past T 21 test results, and a wide geographic range, to capture potential differences in sand and carbon sources.

Table 1. Summary of facilities that were evaluated in this study. Only a subset of the Batch 1 mines was analyzed for Batch 2, due to delays in sample receipt.

Batch 1		Batch 2	
Facility ID	County	Facility ID	County
05045	Glades	05045	Glades
05455	Glades	05455	Glades
GA713	Charlton	GA713	Charlton
76349	Putnam	76349	Putnam
46573	Bay	16564	Polk
50471	Gadsen	16024	Polk
60718	Walton		
11057	Lake		
11298	Lake		
11490 P2	Lake		
36491	Marion		
16608	Polk		

3. METHODS

3.1. AASHTO T 21

The AASHTO T 21 test is officially known as the Standard Method of Test for Organic Impurities in Fine Aggregates for Concrete. In this case, 18 samples of silica sand from soil locations in Florida and Georgia were tested. There are two procedures involved in the development of AASHTO T 21; one uses a glass color standard that references the Gardner Color Scale, and the other uses a standard color solution.

During the first day of testing, each jar was filled with 130 mL of sand using the jar's gradations. Since the soil sand was specified to be measured by volume instead of weight, this may be a step where error can be introduced during the preparation of the test method. However, each sample was measured as equally as possible to avoid lack of precision in the results among each jar. A three percent sodium hydroxide solution was prepared with 30 grams of sodium hydroxide pellets and 1000 mL water. The three percent sodium hydroxide solution was poured into each jar to reach a total volume of 200 mL. Jars were shaken, and more sodium hydroxide solution was added when necessary to reach the 200 mL mark. Samples were kept at room temperature for 24 hours. After 24 hours, the color of the solution in each jar was compared to the Gardner Color Scale, and the Gardner Color Standard number was converted to T 21 values, according to the AASHTO T 21 method. Samples with T 21 values greater than 4 were assigned a "fail," while those with values less than 4 were assigned a "pass."

3.2. AASHTO T 71

Samples were analyzed following the AASHTO T 71 test for 7-day and 28-day strength by the FDOT. Data for each sample was provided by John Shoucair, State Materials Office.

3.3. Total Carbon Determination with the Modified Walkley-Black Method

There are various modified versions of the original Walkley-Black method, which was originally developed in 1947, to quantify the organic matter content in soils. The method used here was based on the Association of Fertilizer and Phosphate Chemists (AFPC) procedure (No. 17 Organic Matter-C), which has been included as a standard operating procedure (SOP) as an appendix to this document.

Prior to the beginning of this test, an aliquot of each of sample was oven dried at 70°C. The weight of each beaker, both empty and with the soil, was taken before and after placing them in the oven for 24 hours at a temperature of 70°C for the purpose of calculating the moisture content of each soil sample. After 24 hours, each sample was weighed, and placed back in the oven and re-weighed until they reached a constant mass. The moisture content in sand was determined by using Equation 1, where MC refers to the percentage moisture content, W_{wet} refers to the initial weight of the sand sample, and W_{dry} refers to the final weight of the sand sample after drying.

$$MC = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \qquad \textbf{Equation 1}$$

The reagents used in the MWB method include 0.2 N potassium dichromate, 1:9 sulfuric acid solution, 0.1 N ferrous ammonium sulfate, 0.5% diphenylamine indicator (DPA), a standard sucrose solution with a concentration of 0.842 mg carbon per mL of solution, concentrated sulfuric acid, and sodium fluoride. All reagents were prepared in the fume hood.

After the reagents were prepared, AFPC's modified version of the Walkley Black test involved the production and analysis of three solutions per sample: a blank sample, a sugar solution sample, and a sand sample. For the sand sample solution, it was determined that 50.0 g of each sand sample would be analyzed to target 5 to 10 mg of organic matter. This amount of sand was weighed and transferred into a 250-mL borosilicate glass beaker. 20 mL of potassium dichromate was poured into the beaker using a 50 mL burette and 30 mL of concentrated sulfuric acid was carefully poured while stirring the solution. This produces an exothermic reaction, so the solution was allowed to cool before proceeding to the next step. Then, 100 mL of deionized water and 5 g of sodium fluoride was added and mixed into the beaker. Before starting the titration of the solution, 2 mL of the diphenylamine was added as an indicator. The sample solution was titrated with ferrous ammonium sulfate solution from a 50-mL burette. A dark grayish-green color in the solution defined the end point of the titration. The process was repeated with both the blank and the sugar standard solution to standardize solutions against each other, before and after testing each soil sample. The blank sample followed the above procedure, but with no sand added, while the test for the sugar standard was conducted with 10 mL of standard sucrose solution in lieu of sand. All other steps of the procedure were as described for the sand sample above and are described in more detail in the SOP included in the appendix.

To determine the percent carbon in the sample, the concentration of reagents between potassium dichromate and ferrous ammonium sulfate, R, needed to be calculated using Equation 2, where A_1 is the volume of potassium dichromate solution in the blank sample and B_1 is the volume of ferrous ammonium sulfate solution in the blank sample. The amount of carbon consumed per volume potassium dichromate, E, in mg C mL^{-1} was calculated using Equation 3, where A_2 and B_2 are the volume of potassium dichromate solution and ferrous ammonium sulfate solution used for the analysis of the sucrose standard, respectively, and D is the volume of standard sucrose solution. The percent carbon in each sample was determined with Equation 4, using the previously calculated values of R and E, the weight of the sample in g, W, and the volumes of potassium dichromate and ferrous ammonium sulfate solution (A and B, respectively) used for the sand sample. Each sample was analyzed three times for the purpose of comparing replicates and precision of results.

$$R = \frac{A_1}{B_1}$$ **Equation 2**

$$E = 0.842 * \frac{D}{[A_2 - (R * B_2)]}$$ **Equation 3**

$$\%C = E * \frac{[A - (R * B)]}{W * 10}$$ **Equation 4**

3.4. Total Carbon Determination via Elemental Analyzer

The combustion method via Elemental Analyzer required less sample preparation than the MWB previously described, but required the use of an elemental analyzer, located at the University of Florida's Stable Isotope Laboratory. Since the elemental analyzer was coupled to an isotope ratio mass spectrometer, samples were also analyzed for the stable isotope value of carbon ($\delta^{13}C$). This value does not provide information regarding the amount of carbon in a sample, but does provide information regarding the origin of carbon in a sample [20].

Triplicate oven dried samples were run for this analysis. This method requires a target weight of 0.2 mg of carbon, and, as such, approximately 20 to 50 mg of sample was analyzed per sample. While larger sample amounts were desired, there are no facilities readily available to receive samples as large as 3 grams at the University of Florida or at other nearby facilities (Dr. J. Curtis, pers. comm.). Sand samples were weighed and added to tin capsules, then each capsule was closed and rolled into a ball and transferred to a 96-well tray. Samples were loaded into the autosampler, and then analyzed with a Carlo Erba 1500 CN elemental analyzer coupled to a Thermo Electron DeltaV Advantage isotope ratio mass spectrometer (Carlo Erba/ThermoFisher Scientific™, Waltham, MA, USA) at UF's Stable Isotope Facility.

3.5. Analysis of Other Elements of Interest

Other elements of interest that may interfere with concrete strength include phosphorus (P), boron (B), and zinc (Zn). The concentration of these elements was also measured to evaluate other constituents that may interfere with concrete setting and strength. Samples were submitted to the University of Florida's Analytical Research Laboratory to evaluate the concentration of these elements with Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) according to EPA method 200.7 [21].

3.6. Isothermal Calorimetry

An eight-channel isothermal calorimeter was used to measure the reaction rate of mortar made with each of the sands. The heat of hydration measured in the isothermal calorimeter is proportional to the cement hydration reaction, and the cumulative heat released during the first several days is proportional to the cement strength gain for a given cement [22]. A cement-sand ratio of 1 was used for the isothermal calorimetry experiments. The sample sand, cement, and water were weighed and placed in a 20 mL ampoule and mixed using a vortex mixer for 60 seconds. After mixing, the samples were placed in the isothermal calorimeter at 73.4°F (23°C). The heat of hydration for each sample was measured for three days.

4. RESULTS AND DISCUSSION

4.1. T 21 and T 71 Results

The T 21 color test results indicated that six of the eighteen samples studied had values greater than or equal to 4 and failed the T 21 test (Table 2). Results from the T 21 color test were highly correlated between labs from the University of Florida and FDOT (r^2=0.96) and both laboratories reached the same conclusion regarding whether samples passed the T-21 test (Figure 1).

Table 2**.** Summary of the T 21 color test results for all samples. Samples with a value of 4 or greater were considered a failing score.

FIRST BATCH				
Facility ID	County	Gardner Color Standard No.	Organic Plate No. (T 21 Value)	T 21 Score
05045	Glades	11	2	Pass
05455	Glades	18	5	Fail
GA713	Charlton	8	1	Pass
76349	Putnam	8	1	Pass
46573	Bay	8	1	Pass
50471	Gadsen	8	1	Pass
60718	Walton	8	1	Pass
11057	Lake	18	5	Fail
11298	Lake	8	1	Pass
11490 P2	Lake	14	3	Pass
36491	Marion	8	1	Pass
16608	Polk	18	5	Fail
SECOND BATCH				
Facility ID	County	Gardner Color Standard No.	Organic Plate No. (T 21 Value)	T 21 Score
05045	Glades	8	1	Pass
05455	Glades	18	5	Fail
GA713	Charlton	18	5	Fail
76349	Putnam	8	1	Pass
16564		16	4	Fail
16024		18	2	Pass
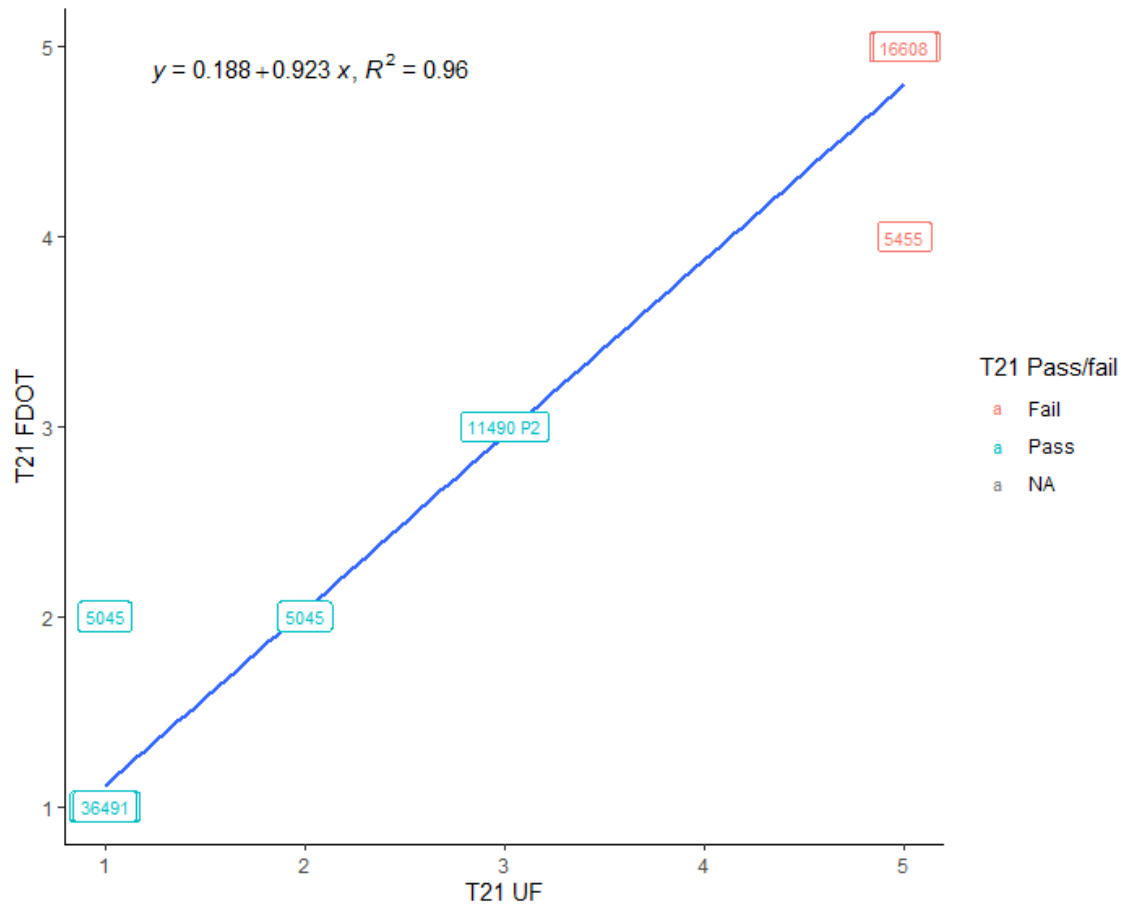
Figure 1. Comparison of T 21 results from the University of Florida (UF) laboratory and the FDOT laboratory. Results were highly correlated (r^2 = 0.96) and both labs reached the same pass/fail score.

The T 21 color test results were evaluated for different regions in Florida. Samples that were collected from central and south Florida scored higher on the color test relative to samples collected in northern Florida (Figure 2). This suggests that the geographic region, and likely underlying geology, may influence the organic matter content of mines throughout Florida.
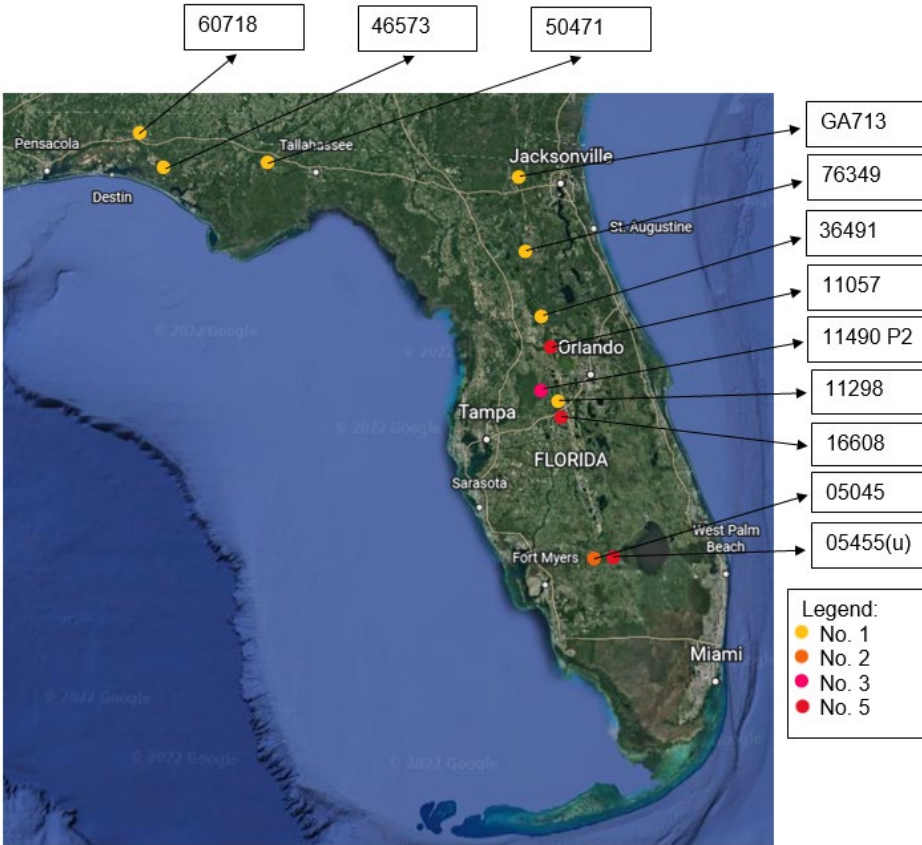
Figure 2. Map of the mines analyzed in Florida and Georgia. Samples are color coded based on their T-21 color test score.

To evaluate whether there was a relationship between the T 21 color results and concrete strength, T 21 and T 71 results were compared, for both 7 day and 28-day strength. There was no relationship between T 21 and T 71 results for either 7-day strength ($r^2=0.08$; Figure 3a) or 28-day strength ($r^2<0.01$; Figure 3b). These findings confirm what was previously known: that samples that score poorly on the T 21 color test can pass the T 71 mortar cube test. Interestingly, there were also samples that had a passing T 21 color value of 1 but failed the T 71 test.

There were also differences between which mines failed the T 71 mortar cube test on day 7, and those that failed the T 71 mortar cube test on day 28. On day 7, mines 76349 (batch 1), 11057 (batch 1), 11298 (batch 1 and 2), and 16608 (batch 2) failed the T 71 mortar cube test, while on day 28, mines 5455 (batch 1), GA713 (batch 1), 76349 (batch 1), and 11298 (batch 1) failed.
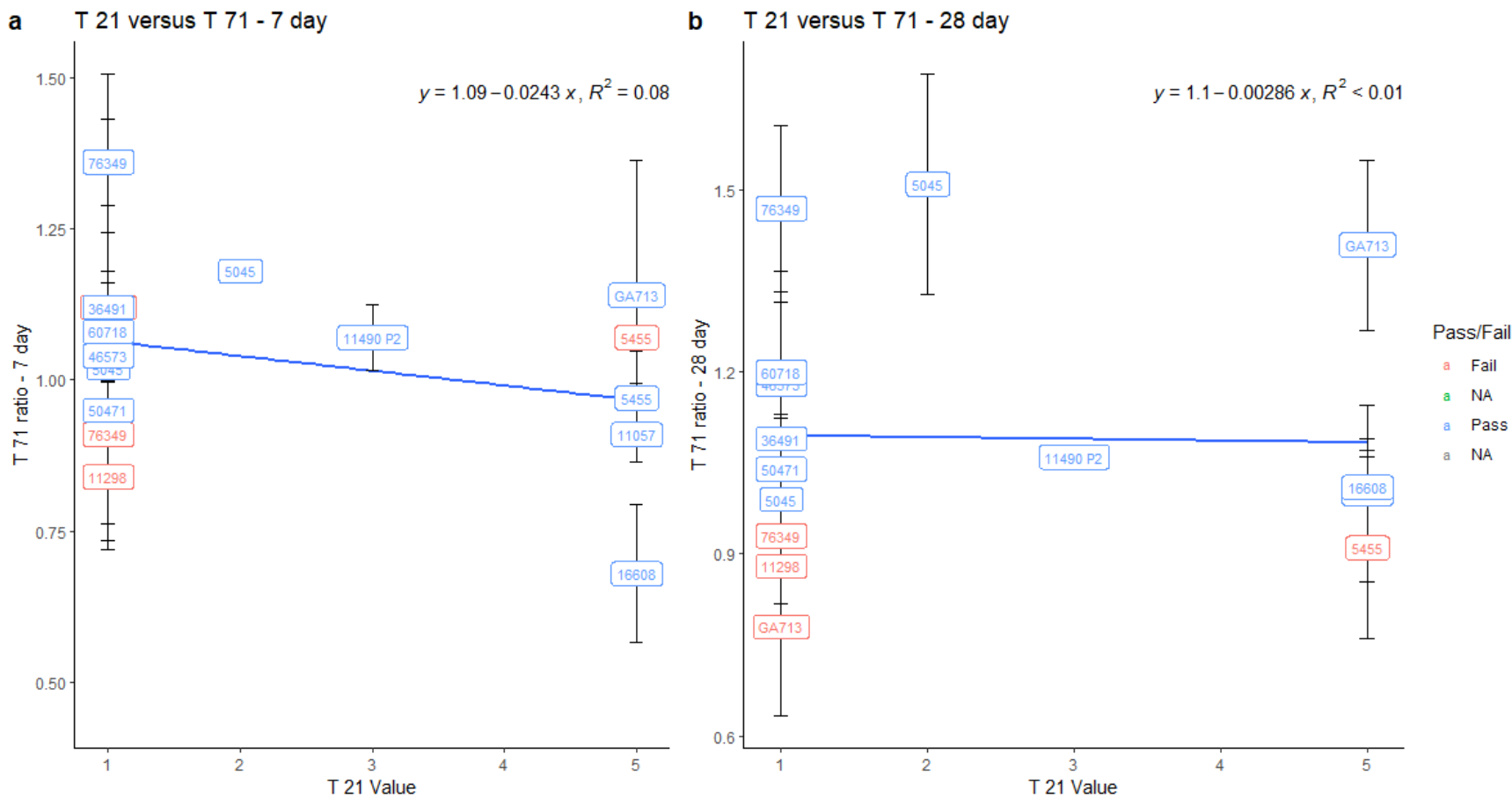
Figure 3. Results from the T 21 color test and the T 71 mortar cube test for (a) 7-day strength and (b) 28-day strength. Each point includes the mine ID, and the color indicates whether the sample passed the T 71 test. Points represent mean values and error bars represent standard deviation. No relationship was seen between the results of the T 21 color test and the T 71 mortar cube test.

4.2. Modified Walkley Black

Based on the MWB method, % total carbon in sand samples ranged from 0.0011% (Mine 76349) to 0.0194% (Mine 05455) (Table 3). For the four mines that were analyzed for both the first and second batch, the relative percent difference (RPD; Equation 5, where x_1 is the value for the first batch and x_2 is the value for the second batch), between the first and second batch was 11.5% for Mine 05045, 19.8% for Mine 05455, 164% for GA713, and 61.9% for Mine 76349, indicating that there is likely temporal variability in the total carbon for each mine. However, these results are to be expected, as mine GA713 has a washing process, and the first sample was taken after the wash process, and the second sample was taken before the wash process. This is in agreement with the T 21 values for Mine GA713, which had a passing T 21 score (1) at the first timepoint but had a failing T 21 score (5) at the second timepoint.

$$R = \frac{x_2 - x_1}{\frac{x_2 + x_1}{2}} \times 100$$ **Equation 5**

Table 3. Modified Walkley Black results for each mine studied. Values are presented for the first and second batch of samples.

FIRST BATCH					
Sample ID	Carbon (%): 1st Replicate	Carbon (%): 2nd Replicate	Carbon (%): 3rd Replicate	Carbon (%): Average	Standard Deviation
05045	0.0049	0.0027	0.0026	0.0034	0.001072
05455	0.0186	0.0201	0.0195	0.0194	0.000599
GA713	0.0019	0.0026	0.0023	0.0023	0.000297
76349	0.0010	0.0011	0.0012	0.0011	9.81E-05
46573	0.0015	0.0020	0.0023	0.0019	0.000337
50471	0.0039	0.0028	0.0030	0.0032	0.00047
60718	0.0047	0.0035	0.0037	0.0040	0.000521
11057	0.0163	0.0144	0.0130	0.0145	0.001359
11298	0.0043	0.0048	0.0048	0.0046	0.000241
11490 P2	0.0057	0.0050	0.0046	0.0051	0.000464
36491	0.0038	0.0037	0.0041	0.0039	0.000186
16608	0.0094	0.0095	0.0094	0.0094	5.18E-05
SECOND BATCH					
Sample ID	Carbon (%): 1st Replicate	Carbon (%): 2nd Replicate	Carbon (%): 3rd Replicate	Carbon (%): Average	Standard Deviation
05045	0.0029	0.0031	0.0054	0.0038	0.001116
05455	0.0229	0.0240	0.0240	0.0237	0.000501
GA713	0.0238	0.0238	0.0238	0.0238	3.52E-05
76349	0.0014	0.0014	0.0036	0.0021	0.001019

16564	0.0036	0.0042	0.0046	0.0041	0.000439
16024	0.0030	0.0033	0.0024	0.0029	0.000373

4.3. Elemental analysis

Based on the Elemental analysis method, the total carbon values were from 0.01% (Mine 50471) to 0.12% (Mine 05045) (Table 3). Total carbon values measured by EA were greater than those estimated by the MWB method. Despite this, a positive relationship was seen between MWB and EA results, although there was one outlier (Mine 05045), which resulted in a low r^2 value of 0.15 (Figure 4a). When this mine was removed, the MWB and EA results were highly correlated ($r^2 = 0.78$; Figure 4b). Total inorganic carbon (TIC) was also analyzed for each sample to determine if any inorganic carbon was present in the samples. All samples had undetectable amounts of inorganic carbon, confirming that the total carbon values measured via EA reflected only organic carbon for these samples.

Table 4. Elemental analysis results for each mine studied. Values are presented for the first and second batch of samples.

FIRST BATCH				
Sample ID	Carbon (%): 1st Replicate	Carbon (%): 2nd Replicate	Carbon (%): 3rd Replicate	Carbon (%): Average	Standard Deviation
05045	0.12	0.08	0.15	0.12	-0.04
05455	0.12	0.05	0.07	0.08	-0.04
GA713	0.04	0.03	0.03	0.03	-0.01
76349	0.02	0.02	0.02	0.02	0
46573	0.02	0.01	0.01	0.01	-0.01
50471	0.01	0.01	0.01	0.01	0
60718	0.02	0.02	0.02	0.02	0
11057	0.05	0.04	0.04	0.04	-0.01
11298	0.02	0.02	0.03	0.02	-0.01
11490 P2	0.02	0.02	0.03	0.02	-0.01
36491	0.02	0.02	0.02	0.02	0
16608	0.02	0.03	0.03	0.03	-0.01

a

$y = 0.0236 + 2.16\,x,\ R^2 = 0.15$

EA Total Carbon (%)

Modified Walkley Black Total Carbon (%)

5045
5455
11057
GA713
16608
11490 P2
76349
36491
46573
50471

b

$y = 0.00982 + 2.96\,x,\ R^2 = 0.78$

EA Total Carbon (%)

Modified Walkley Black Total Carbon (%)

5455
11057
GA713
16608
11490 P2
76349
36491
46573
50471
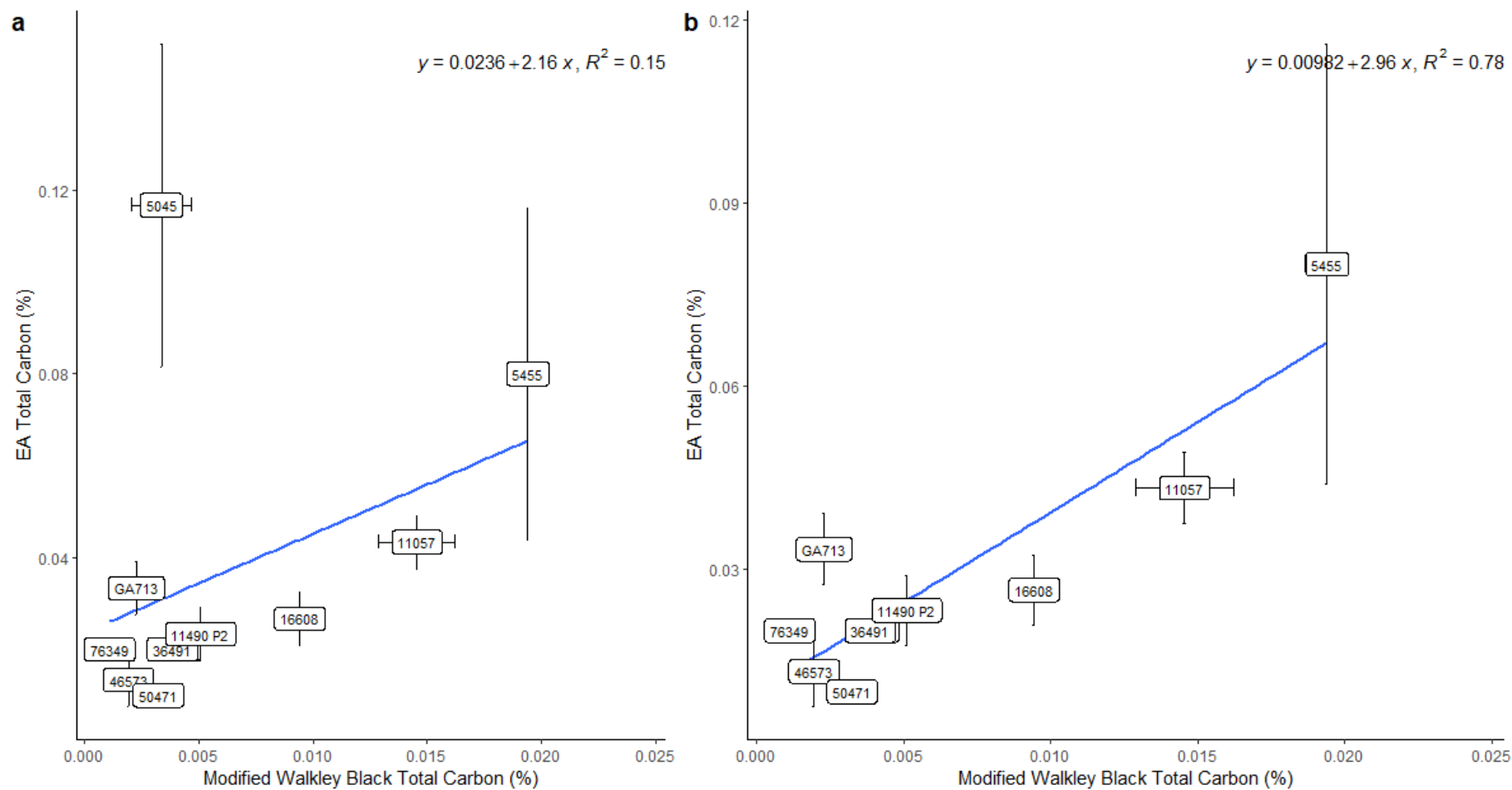
Figure 4. Comparison of total carbon (%) as determined via Modified Walkley Black (MWB) and elemental analysis (EA). Points represent mean values and error bars represent standard deviation. Data are presented for (a) all samples, and (b) without mine 05045.

4.4. Relationships Between Carbon Content and T 71 Mortar Cube Tests

There was a positive relationship between total carbon content (as measured by the MWB method) and T 21 color results (Figure 5). The positive relationship between the MWB test and T 21 results, indicates that the MWB method reliably quantifies carbon content. However, there appeared to be no relationship between organic carbon content (as measured by the MWB method) and the T 71 results, for either 7-day (Figure 6a) or 28-day (Figure 6b) strength. This lack of relationship indicates that there are likely other factors, aside from total carbon content, that result in a loss of concrete strength. Some other factors to consider are the type of carbon that is in the sample, as well as the presence of other interfering compounds that may reduce concrete strength.
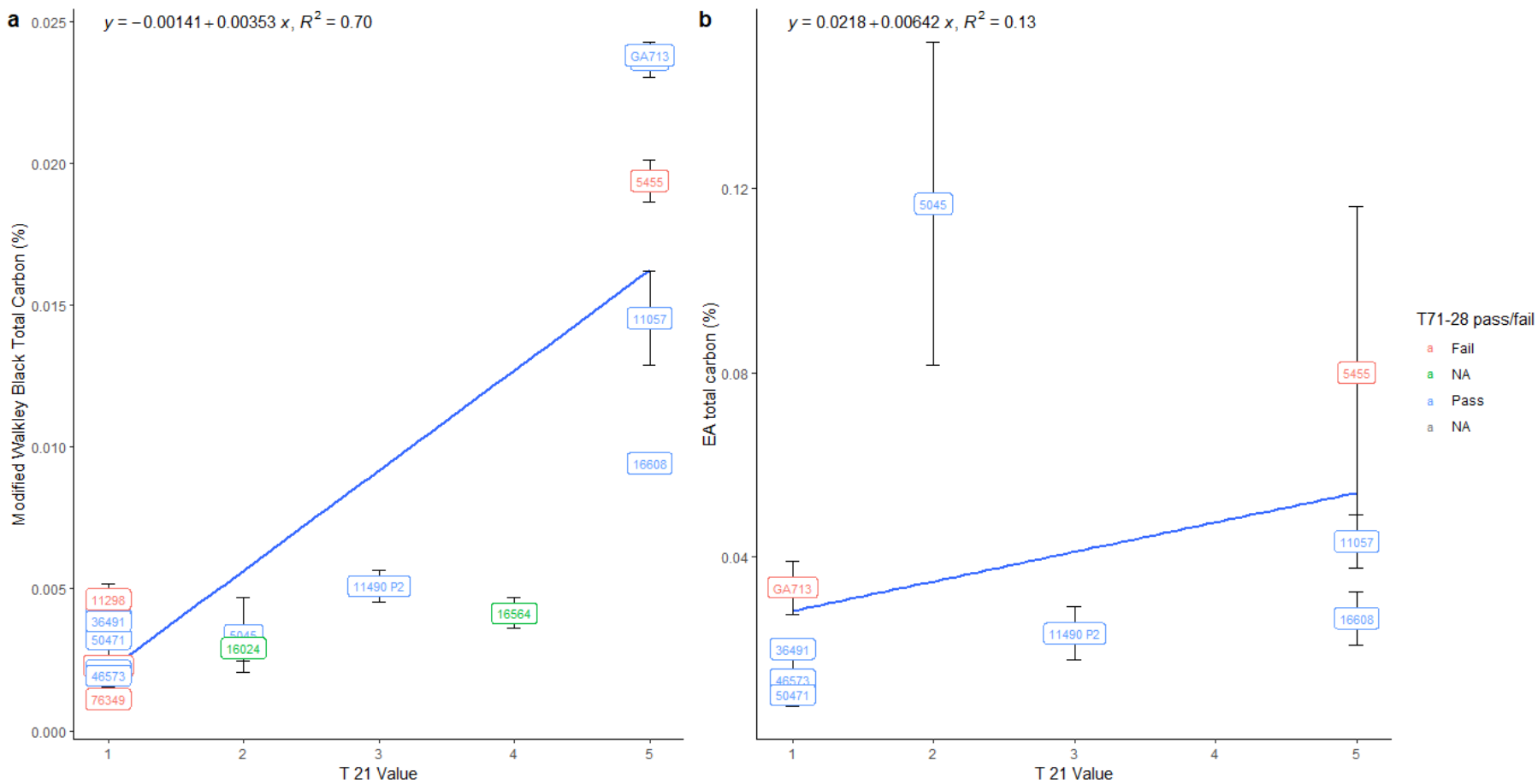
Figure 5. Results from the T 21 color test, compared to total carbon as determined by the Modified Walkley Black method and Elemental Analysis (EA). Each point includes the mine ID, and the color indicates whether the sample passed the T 71 test at 28 days. Samples in green were not analyzed for the T 71 test.

Figure 6. Results from the Modified Walkley Black (MWB) method (% total carbon) and the T 71 mortar cube test for (a) 7-day strength and (b) 28-day strength. Each point includes the mine ID, and the color indicates whether the sample passed the T 71 test. No relationship was seen between % total carbon as measured by the MWB test and concrete strength as measured by the T 71 mortar cube test. The horizontal red line is the 0.95 cutoff.

There was a slightly positive relationship between total carbon determined via EA and T 71 results for day 7 and day 28, however, it was a weak relationship that is likely not meaningful (Figure 7).

Interestingly, there was a positive relationship between the $\delta^{13}C$ value of sand samples and the T 71 7-day mortar cube strength ($r^2=0.42$). However, this relationship was not seen with the T 71 28-day strength tests. Samples that failed the 7-day strength test tended to have lower $\delta^{13}C$ values. This may indicate that the source of carbon [20] may influence concrete strength in its early stages, but further investigation is needed.

a EA (%C) versus T 71 - 7 day

$y = 0.952 + 1.61\,x,\ R^2 = 0.14,\ P = 0.258$

b EA (%C) versus T 71 - 28 day

$y = 0.969 + 2.58\,x,\ R^2 = 0.20,\ P = 0.172$
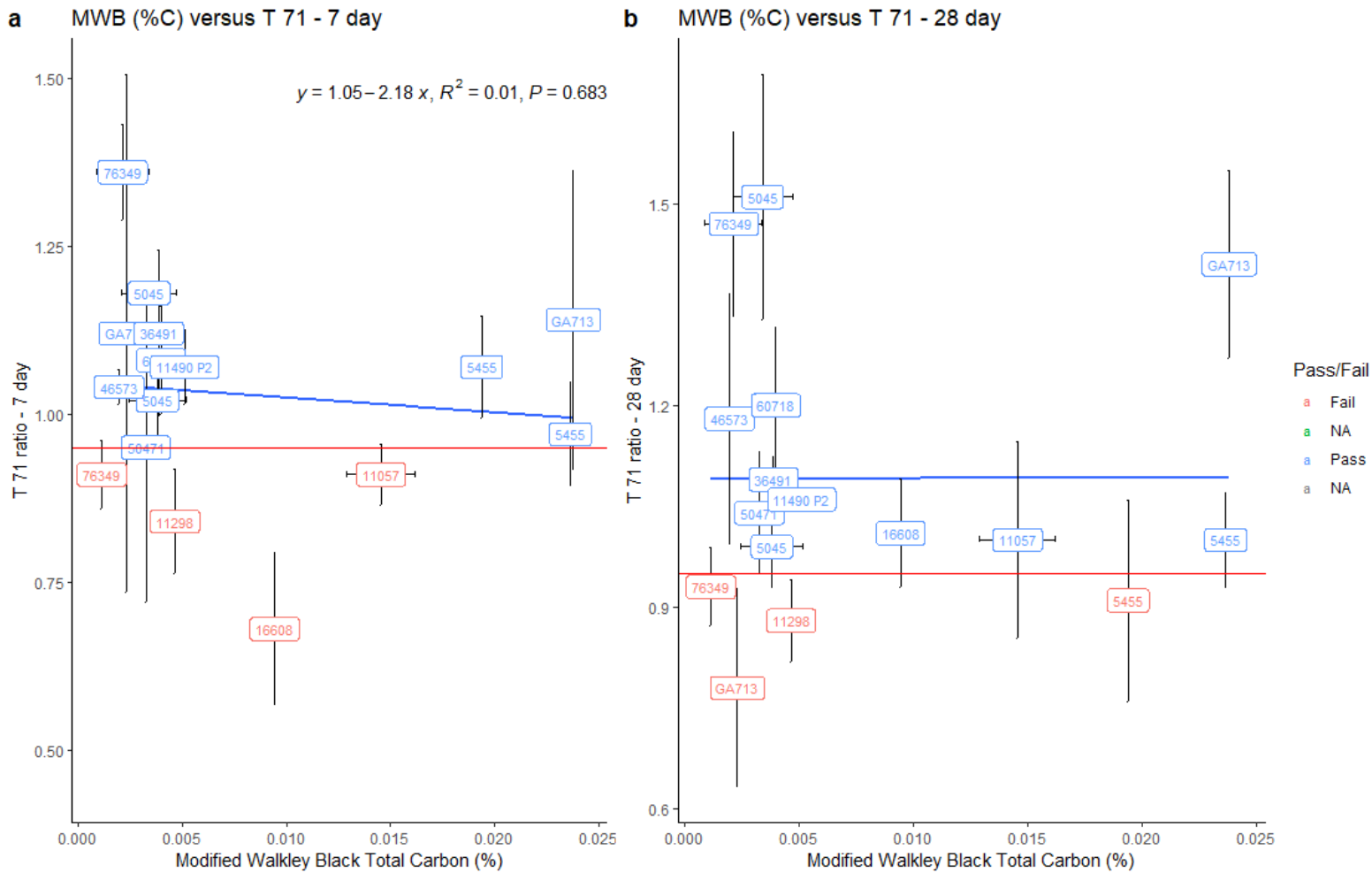
Pass/Fail

a Fail
a NA
a Pass
a NA
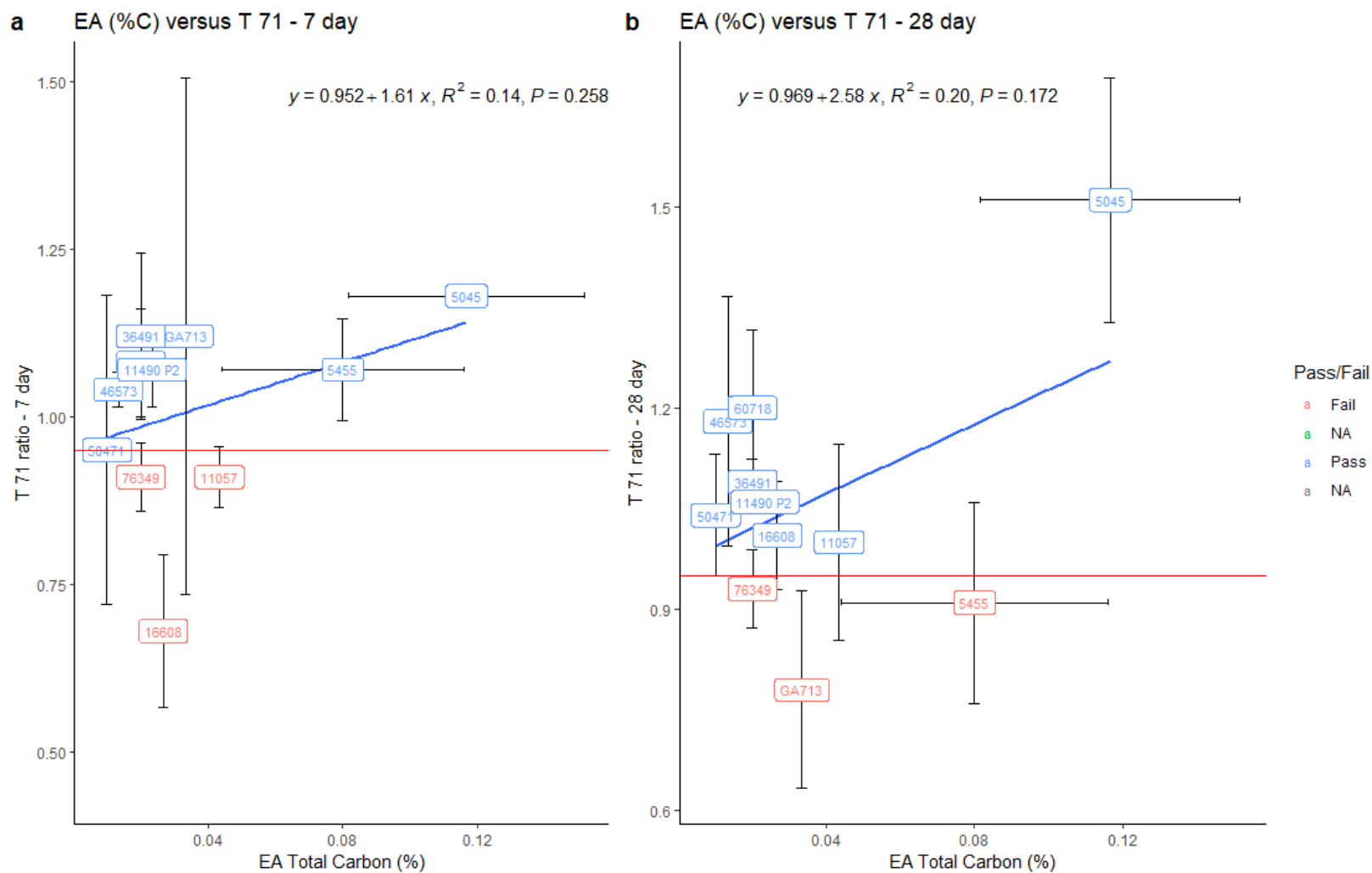
Figure 7. Results from the Elemental Analysis (EA) method (% total carbon) and the T 71 mortar cube test for (a) 7-day strength and (b) 28-day strength. Each point includes the mine ID, and the color indicates whether the sample passed the T 71 test. There as a slight positive relationship between % total carbon as determined via EA and the T 71 test, but this was a weak relationship. The horizontal red line is the 0.95 cutoff.

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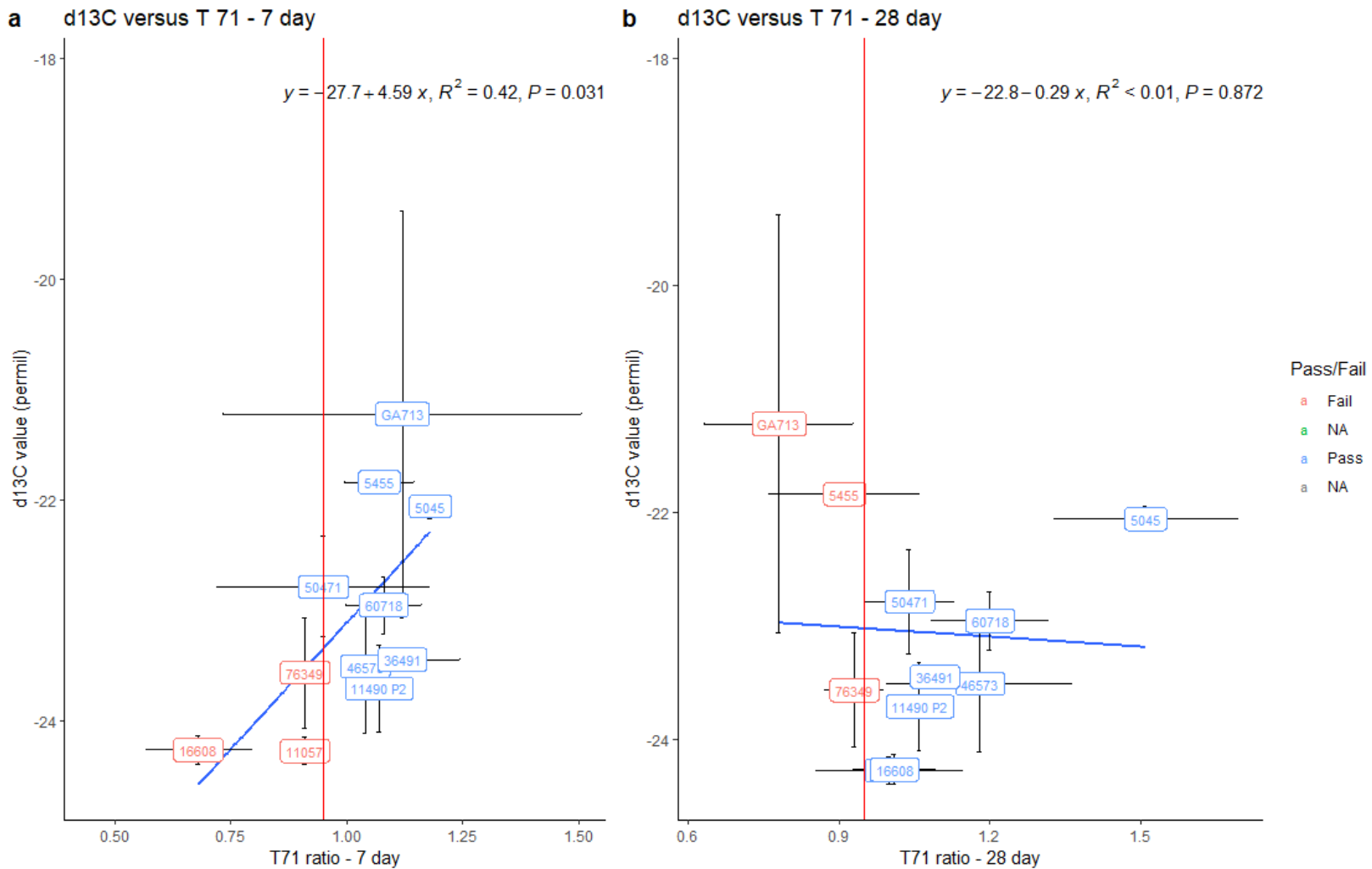
Figure 8. Results from the $\delta^{13}C$ value of sand samples and the T 71 mortar cube test for (a) 7-day strength and (b) 28-day strength. Each point includes the mine ID, and the color indicates whether the sample passed the T 71 test. A positive relationship was seen between the $\delta^{13}C$ value of sand samples and the T 71 ratio at 7 days, suggesting that the type and/or source of carbon may influence early cement hydration. The vertical red line is the 0.95 cutoff.

4.5. Inductively Coupled Plasma – Atomic Emission Spectrometry

In all samples, Boron was not detectable (i.e. values < the minimum detection limit), and Zinc was only detectable in one sample (GA713; 0.6 mg kg^{-1}). Phosphorus was within detection limits for all samples. A very weak negative relationship was seen between phosphorus and T 71 7 day and 28-day strength (Figure 9). This slight negative relationship may indicate that phosphorus may negatively influence concrete strength, however, additional investigation is needed to confirm this.

a Phosphorus versus T 71 - 7 day

$y = 1.08 - 0.00286\,x,\ R^2 = 0.11,\ P = 0.201$

b Phosphorus versus T 71 - 28 day

$y = 1.15 - 0.00309\,x,\ R^2 = 0.07,\ P = 0.318$

Pass/Fail

a Fail
a NA
a Pass
a NA

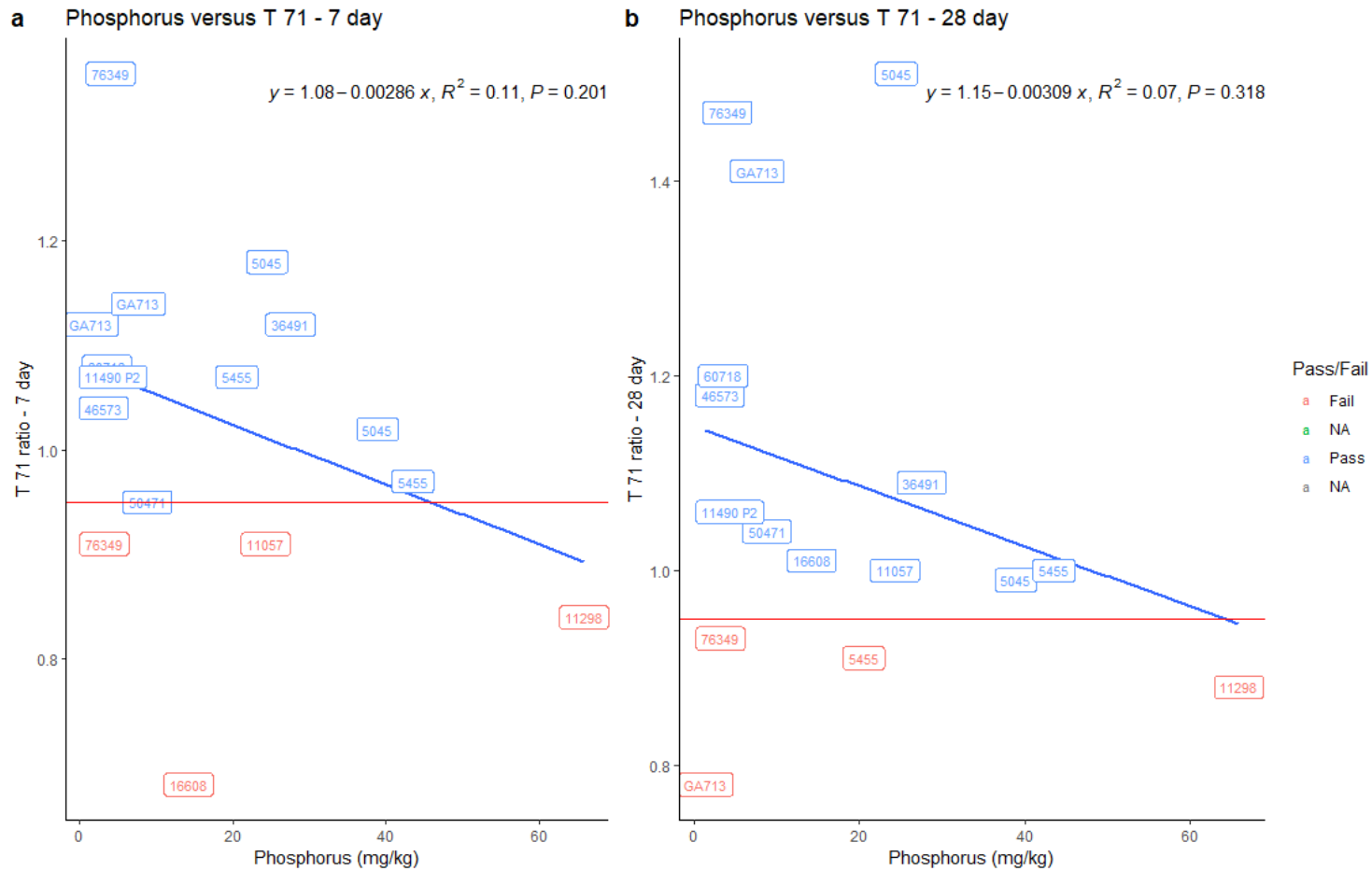Figure 9. Phosphorus content and the T 71 mortar cube test results for (a) 7-day strength and (b) 28-day strength. Each point includes the mine ID, and the color indicates whether the sample passed the T 71 test. A slight negative relationship was seen between the phosphorus content of sand samples and the T 71 ratio, suggesting that phosphorus content may decrease cement strength. The horizontal red line is the 0.95 cutoff.

4.6. Isothermal Calorimetry

Isothermal calorimetry was performed on mortar samples made with Ottawa sand as a control sand and with the sand samples studied. The heat of hydration rate and cumulative heat of hydration for each mixture were calculated. Figure 10 shows the heat of hydration rate measured for the control sand and sand 05455 from both the first and second batches with time. Very little difference was seen in the time when the cement hydration acceleration period began, indicating that any organics present in the sample did not significantly retard the cement hydration reaction. Figure 11 shows the cumulative heat of hydration for the same mortar mixtures shown in Figure 10. Table 5 shows the 48-hour cumulative heat of hydration for each sample tested. The single operator precision for cumulative heat of hydration at 2 days is 3.2%. Aside from values measured for 05455 and 76349 where one of the replicates for each were unusually low and likely outliers, none of the sands had statistically different heat of hydration values from the control Ottawa sand. The isothermal calorimetry results suggest that because the organic material is not significantly affecting the cement hydration, it may be causing air entrainment stabilization that could reduce strength, or issues with the variability in the mortar cubes.
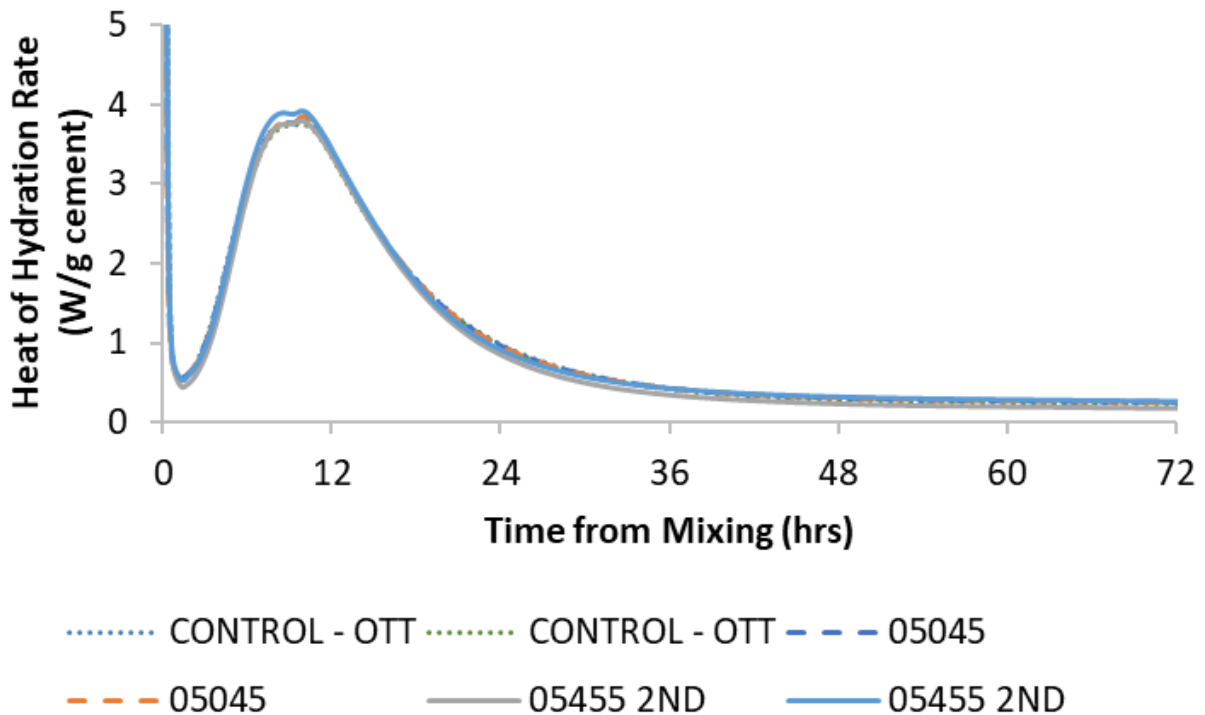

Figure 10. Isothermal heat of hydration rate for mortar samples made with control Ottawa sand, the first batch of 05455 sand, and the second batch of 05455 sand.
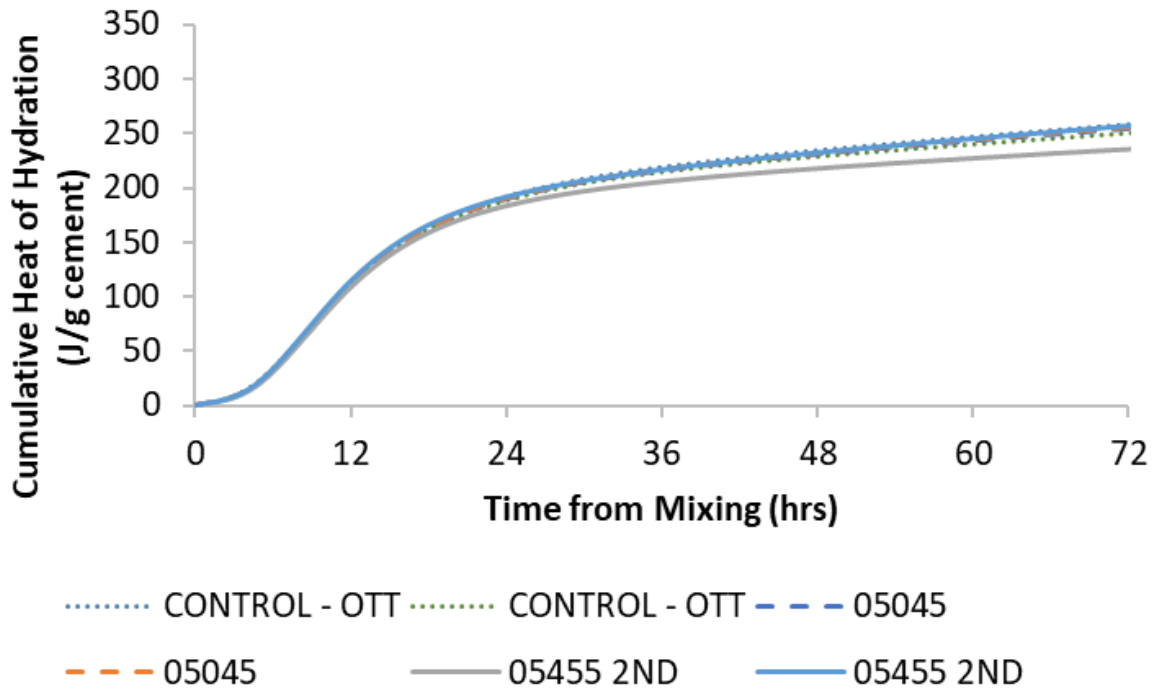
Figure 11. Cumulative isothermal heat of hydration for mortar samples made with control Ottawa sand, the first batch of 05455 sand, and the second batch of 05455 sand.

Table 5. Mortar 48 hour heat of hydration values.

Batch	Sand Sample	Replicate 1	Replicate 2
First	Control Ottawa Sand	234.5	230.0
	05045	225.3	229.2
	05455	231.4	231.4
	GA713	234.4	234.8
	76349	231.4	234.0
	46573	230.3	232.0
	50471	232.5	231.4
	60718	232.9	232.5
	11057	230.5	232.7
	11298	230.8	230.0
	11490 P2	-	223.4
	36491	234.0	232.2
	16608	231.8	232.3
Second	05045	232.7	232.7
	5455	218.3	232.2
	GA713	231.9	230.6
	76349	227.1	218.2
	16564	231.9	227.6
	16024	232.3	230.5

5. CONCLUSIONS

A literature and industry review was conducted to identify tests to quantify the amount of total carbon in a sand sample. The Modified Walkley Black method and Elemental analysis via combustion were both identified as tests that could be performed quickly (< 5 days) and affordably (< $100/test), thereby meeting the criteria for speed and affordability. Sands from mines throughout Florida and Georgia were tested with these two methods to evaluate their performance in relation to the AASHTO T 21 color test and the AASHTO T 71 mortar cube test. Mines were selected to encompass a range of T 21 scores, and to represent many different regions throughout Florida.

The MWB method and EA method were in general agreement regarding total carbon content, with the exception of mine 05045. It was also noted that there was temporal variability in the carbon content of each mine, based on the T 21 color tests and MWB results, highlighting the need for continued monitoring, rather than one timepoint.

While tests were found that could meet the cost and time requirements, there did not appear to be a relationship between the % total carbon of a sand sample (either via the MWB or EA method), with concrete strength, as measured by the T 71 mortar cube test (either 7-day or 28-day). The lack of relationship between the total carbon content and the T 71 mortar cube test suggest that

either the type of carbon or other interfering compounds may reduce concrete strength, rather than total carbon. Additional analyses were conducted to investigate other mechanisms that might interfere with concrete strength. A positive relationship between $\delta^{13}C$ values and T 71 mortar cube test results was found, which may indicate that the source/type of carbon influences early cement hydration processes. Additionally, there was a slightly negative relationship between phosphorus content and the T 71 mortar cube test results (for both day 7 and day 28), suggesting that phosphorus may interfere with concrete strength. However, this relationship was weak, and further investigation is needed.

Based on the results of these tests, either the Modified Walkley Black or Elemental Analysis can be recommended to reliably determine the total carbon in a sand sample. However, neither test was related to T 71 test results, indicating that these tests are not suitable for replacing AASHTO T 71.

6. REFERENCES

[1]   S. Mindess and J. F. Young, *Concrete*. Prentice Hall, 2002.

[2]   J. K. Norvell, J. G. Stewart, M. C. G. Juenger, and D. W. Fowler, "Influence of Clays and Clay-Sized Particles on Concrete Performance," *Journal of Materials in Civil Engineering*, vol. 19, no. 12, Dec. 2007, doi: 10.1061/ASCE0899-1561200719:121053.

[3]   Claire, K. E., & Sherwood, P. T. (1954). The Effect Of Organic Matter On The Setting Of Soil - Cement Mixtures. Journal of Applied Chemistry, 4(11), 625–630.

[4]   F. F. Ataie, M. C. G. Juenger, S. C. Taylor-Lange, and K. A. Riding, "Comparison of the retarding mechanisms of zinc oxide and sucrose on cement hydration and interactions with supplementary cementitious materials," *Cem Concr Res*, vol. 72, pp. 128–136, 2015, doi: 10.1016/j.cemconres.2015.02.023.

[5]   A. S, M. T. Moses, L. Bennet Thomas, J. Scaria, and G. v Dev, "Prospective Benefits Of Using Activated Carbon In Cement Composites - An Overview," *International Journal of Civil Engineering and Technology (IJCIET)*, vol. 10, no. 3, pp. 2103–2110, 2019.

[6]   T. S. Bianchi, "Estuarine Chemistry," in *Estuarine Ecology*, 2nd ed., J. W. Day Jr, B. C. Crump, W. M. Kemp, and A. Yanez-Arancibia, Eds. Hoboken: John Wiley & Sons, Inc, 2012.

[7]   N. C. Brady, R. R. Weil, and R. R. Weil, *The nature and properties of soils* , vol. 13. Upper Saddle River, NJ: Prentice Hall, 2008.

[8]   M. Kleber and J. Lehmann, "Humic Substances Extracted by Alkali Are Invalid Proxies for the Dynamics and Functions of Organic Matter in Terrestrial and Aquatic Ecosystems," *J Environ Qual*, vol. 48, no. 2, pp. 207–216, Mar. 2019, doi: 10.2134/jeq2019.01.0036.

[9]   H. Tremblay, J. Duchesne, J. Locat, and S. Leroueil, "Influence of the nature of organic compounds on fine soil stabilization with cement," *Canadian Geotechnical Journal*, vol. 39, no. 3, pp. 535–546, 2002, doi: 10.1139/t02-002.

[10]   D. A. Abrams, *Effect of Tannic Acid on the Strength of Concrete*, vol. 7. Structural materials research laboratory., 1922.

[11]   W. H. Kuenning, "Resistance of Portland Cement Mortar to Chemical Attack-A Progress Report," Skokie, Illinois, 1966.

[12]   J. W. Bullard *et al.*, "Mechanisms of cement hydration," *Cement and Concrete Research*, vol. 41, no. 12. pp. 1208–1223, Dec. 2011. doi: 10.1016/j.cemconres.2010.09.011.

[13]   R. Mydal, H. Justnes, and T. Arne Hammer, *Advanced cementing materials - Controlling hydration development - Retarding admixtures for concrete - State of the art*, vol. 3D006020. SINTEF Building And Infrastructure, 2007. [Online]. Available: www.sintef.no/coin

[14]   M. C. Garci Juenger and H. M. Jennings, "New insights into the effects of sugar on the hydration and microstructure of cement pastes," *Cem Concr Res*, vol. 32, no. 3, pp. 393–399, Mar. 2002, doi: 10.1016/S0008-8846(01)00689-5.

[15]   S. Ahmad, A. Lawan, and M. Al-Osta, "Effect of sugar dosage on setting time, microstructure and strength of Type I and Type V Portland cements," *Case Studies in Construction Materials*, vol. 13, Dec. 2020, doi: 10.1016/j.cscm.2020.e00364.

[16]   S. Ge, Y. Pan, L. Zheng, and X. Xie, "Effects of organic matter components and incubation on the cement-based stabilization/solidification characteristics of lead-contaminated soil," *Chemosphere*, vol. 260, Dec. 2020, doi: 10.1016/j.chemosphere.2020.127646.

[17]   N. L. Thomas and J. D. Birchall, "The retarding action of sugars on cement hydration," 1983.

[18]   "AASHTO T 21: Standard Method of Test for Organic Impurities in Fine Aggregates for Concrete," in *American Association of State Highway and Transportation Officials*, Washington D.C., 2020, p. 5.

[19]   N. Li *et al.*, "Quantifying the carbon content of aeolian sediments: Which method should we use?," *Catena*, vol. 185. Elsevier B.V., Feb. 01, 2020. doi: 10.1016/j.catena.2019.104276.

[20]   Lamb, A. L., Wilson, G. P. & Leng, M. J. A review of coastal palaeoclimate and relative sea-level reconstructions using δ13C and C/N ratios in organic material. *Earth-Science Reviews* 75, 29-57 (2006).

[21]   USEPA, U. Method 200.7: determination of metals and trace elements in water and wastes by inductively coupled plasma-atomic emission spectrometry. Rev. 4.4; EPA600/R-94-111 (1994).

[22]   Baran, T., & Pichniarczyk, P. (2017). Correlation factor between heat of hydration and compressive strength of common cement. *Construction and Building Materials*, 150, 321-332.

7. APPENDIX

MODIFIED WALKLEY BLACK SOP

SCOPE:

This Standard Operation Procedure (SOP) covers the steps to perform the Modified Walkley-Black according to Test No. 17 Organic Matter C [1], including sample and reagents preparation. This test primarily covers the quantification of organic matter in sand.

EQUIPMENT:

- Fume hood

MATERIALS
- 3 Volumetric flasks (1000 mL) / batch
- 1 amber bottle (150 mL) / batch
- 1 Volumetric flask (25 mL) / batch
- 2 Burettes (50 mL) / batch
- 1 Borosilicate glass beaker (250 mL) / sample
- Weigh boat
- 1 Scoopula
- 1 Graduated cylinder (100 mL) / batch
- 2 Burette stands / batch
- 2 Clams (minimum) / batch
- 2 Funnels / batch

REAGENTS PREPARATION

All reagents should be prepared in a fume hood.
All references to water refer to deionized water.
Always add acid to water

1. *Potassium dichromate, 0.2 N:*
   Weigh 9.807 g of potassium dichromate into a weigh boat. Add approximately 500 mL of water into a 1000 mL volumetric flask. In a fume hood, add the potassium dichromate to the water and dissolve. Add water to reach a final volume of 1000 mL.

2. *1:9 sulfuric acid solution:*
   Add approximately 500 mL of deionized water to a 1000 mL volumetric flask. Measure 100 mL of concentrated sulfuric acid in a graduated cylinder. Add 100 mL of concentrated sulfuric acid from the graduated cylinder to the flask and dissolve. Add water to bring to a final volume of one liter. Note: volumetric flask will get warm from the reaction.

3. *Ferrous ammonium sulfate, 0.1 N:*
   Add approximately 500 mL of 1:9 sulfuric acid solution to a 1,000 mL volumetric flask. Weigh 39.216 g of ferrous ammonium sulfate in a weigh boat. Add to the volumetric flask and bring to a final volume of one liter with the 1:9 sulfuric acid solution.

4. *Diphenylamine indicator DPA, 0.5%:*
   Weigh 0.5 g of DPA and add it to a 150 mL bottle. Measure 100 mL of concentrated sulfuric acid in a graduated cylinder. Add 100 mL of concentrated sulfuric acid (96-98.3%) from the graduated cylinder to the bottle and dissolve.

5. *Standard sucrose solution:*
   Add approximately 100 mL of water to a 250 mL volumetric flask. Weigh 0.5 g of sucrose and transfer it to the volumetric flask. Bring to a final volume of 250 mL and dissolve.

6. *Concentrated sulfuric acid.*

7. *Sodium fluoride.*

JOB STEPS

Blank Sample:

Get an empty 250-mL borosilicate glass beaker to start the test as a blank sample. Run this blank sample before each test to standardize solutions against each other.

Fill one 50 mL burette with 30 mL of 0.2 N potassium dichromate and add 20 mL to the empty beaker.

Measure 30 mL of 1:9 sulfuric acid in a 50 mL burette. Cautiously, add 30 mL of 1:9 sulfuric acid to the beaker while swirling. Allow solution to cool and add 100 mL of water. Add 5 g of sodium fluoride and mix.

Add 2 mL of the 0.5% diphenylamine to the beaker, to be used as an indicator.

Fill another 50 mL burette with 0.1 N ferrous ammonium sulfate solution and use it to titrate the solution in the beaker, The end point is reached when the purple color disappears, and a dark grayish-green color appears.

If over titration happens, use the burette with 0.2 N potassium dichromate to add enough potassium dichromate to change solution back to deep purple and record amount added, then titrate again to desired green color.

Sugar Solution Sample:

Add 10 mL of standard sugar solution into a 250-mL borosilicic glass beaker, and then analyze using the steps 2-5.

Soil Sample:

Weigh sample containing 5-10mg of organic matter and transfer into a 250-mL borosilicate glass beaker.

Repeat steps 2-5 to analyze the sample.

Determining Organic matter content:

Determine the concentration ratio R of the potassium dichromate.

Determine the mg of carbon consumed per potassium dichromate solution.

Calculate the percent carbon in the sample.

Repeat the procedures for the blank and the standard sugar solution after each test.

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STANDARD OPERATION PROCEDURE FOR
MODIFIED WALKLEY BLACK TEST TO DETERMINE ORGANIC MATTER CONTENT IN SAND

SCOPE:

This Standard Operation Procedure (SOP) covers the steps to perform the Modified Walkley-Black according to Test No. 17 Organic Matter C [1], including sample and reagents preparation. This test primarily covers the quantification of organic matter in sand.

EQUIPMENT:

- Fume hood

MATERIALS
- 3 Volumetric flasks (1000 mL) / batch
- 1 amber bottle (150 mL) / batch
- 1 Volumetric flask (25 mL) / batch
- 2 Burettes (50 mL) / batch
- 1 Borosilicate glass beaker (250 mL) / sample
- Weigh boat
- 1 Scoopula
- 1 Graduated cylinder (100 mL) / batch
- 2 Burette stands / batch
- 2 Clams (minimum) / batch
- 2 Funnels / batch

SAFETY:

This procedure identifies possible safety concerns associated with performing duties covered in the SOP as indicated by:

➢ *Warning* – Warnings are given relating to personal safety issues that may cause physical injury to persons performing a task and/or others around them.

Caution – Cautions are given relating to equipment and/or sample issues that may cause damage to or adversely affect the equipment, sample and/or test results.

Always consult the Safety Data Sheet (SDS) prior to handling chemical admixtures and other construction materials.

GENERAL SAFETY NOTES:

- *Warning* – Potassium dichromate is considered hazardous by the 2012 OSHA Hazardous Communication Standard. This chemical is toxic if swallowed, fatal if inhaled, may intensify fire (oxidizer), and may cause respiratory problems, skin reaction (irritant), or cancer (carcinogen).
- *Warning* **–** Sulfuric acid is known to be corrosive to metals, causes skin corrosion, eye damage, and carcinogenicity.
- *Warning* – Sodium fluoride is a chemical of acute toxicity; it is toxic if swallowed and causes skin and eye irritation.
- *Warning* – Diphenylamine-4-sulfonic acid and ammonium ferrous sulphate are both irritant chemicals, which may cause skin, eye, or respiratory irritation.
- *Warning* – Even though sucrose has not been classified as hazardous according to the Globally Harmonized System of Classification and Labeling of Chemicals, it is important to not breath dust, get in eyes, on skin, or on clothing.
- *Warning* - As with most hazardous chemicals, always wear protective gloves, clothing/eye protection, wash hands thoroughly after handling, avoid breathing dust/fume/gas, use outdoors or in well-ventilated area (use of fume hood is required). Store in a chemical cabinet according to EH&S guidelines, and review necessary safety data sheets for general use, emergency measures, and storage.

Caution - All other safety rules for the lab remain in place while using this equipment. Disregarding any safety rules in place will result in immediate loss of laboratory privileges and disciplinary action.

REFERENCE DOCUMENTS:

[1] Methods of Analysis for Phosphate Rock No. 17 Organic Matter-C

REAGENT PREPARATION

All reagents should be prepared in a fume hood.
All references to water refer to deionized water.
Always add acid to water

8. *Potassium dichromate, 0.2 N:*
    Weigh 9.807 g of potassium dichromate into a weigh boat. Add approximately 500 mL of water into a 1000 mL volumetric flask. In a fume hood, add the potassium dichromate to the water and dissolve. Add water to reach a final volume of 1000 mL.

9. *1:9 sulfuric acid solution:*
    Add approximately 500 mL of deionized water to a 1000 mL volumetric flask. Measure 100 mL of concentrated sulfuric acid in a graduated cylinder. Add 100 mL of concentrated sulfuric acid from the graduated cylinder to the flask and dissolve. Add water to bring to a final volume of one liter. Note: volumetric flask will get warm from the reaction.

10. *Ferrous ammonium sulfate, 0.1 N:*
    Add approximately 500 mL of 1:9 sulfuric acid solution to a 1,000 mL volumetric flask. Weigh 39.216 g of ferrous ammonium sulfate in a weigh boat. Add to the volumetric flask and bring to a final volume of one liter with the 1:9 sulfuric acid solution.

11. *Diphenylamine indicator DPA, 0.5%:*
    Weigh 0.5 g of DPA and add it to a 150 mL bottle. Measure 100 mL of concentrated sulfuric acid in a graduated cylinder. Add 100 mL of concentrated sulfuric acid (96-98.3%) from the graduated cylinder to the bottle and dissolve.

12. *Standard sucrose solution:*
    Add approximately 100 mL of water to a 250 mL volumetric flask. Weigh 0.5 g of sucrose and transfer it to the volumetric flask. Bring to a final volume of 250 mL and dissolve.

13. *Concentrated sulfuric acid.*

14. *Sodium fluoride.*

JOB STEPS

Blank Sample:

Get an empty 250-mL borosilicate glass beaker to start the test as a blank sample. Run this blank sample before each test to standardize solutions against each other.

Fill one 50 mL burette with 30 mL of 0.2 N potassium dichromate and add 20 mL to the empty beaker.

Measure 30 mL of 1:9 sulfuric acid in a 50 mL burette. Cautiously, add 30 mL of 1:9 sulfuric acid to the beaker while swirling. Allow solution to cool and add 100 mL of water. Add 5 g of sodium fluoride and mix.

Add 2 mL of the 0.5% diphenylamine to the beaker, to be used as an indicator.

Fill another 50 mL burette with 0.1 N ferrous ammonium sulfate solution and use it to titrate the solution in the beaker, The end point is reached when the purple color disappears, and a dark grayish-green color appears.

If over titration happens, use the burette with 0.2 N potassium dichromate to add enough potassium dichromate to change solution back to deep purple and record amount added, then titrate again to desired green color.

Sugar Solution Sample:

Add 10 mL of standard sugar solution into a 250-mL borosilicic glass beaker, and then analyze using the steps 2-5.

Soil Sample:

Weigh sample containing 5-10mg of organic matter and transfer into a 250-mL borosilicate glass beaker.

Repeat steps 2-5 to analyze the sample.

Determining Organic matter content:

Determine the concentration ratio R of the potassium dichromate.

Determine the mg of carbon consumed per potassium dichromate solution.

Calculate the percent carbon in the sample.

Repeat the procedures for the blank and the standard sugar solution after each test.

FORMULAS

Concentration ratio of reagents:

$$R = \frac{A1}{B1}$$

Mg of carbon consumed per potassium dichromate solution:

$$E = 0.842 * \frac{D}{[A2 - (R * B2)]}$$

Percent carbon in the sample:

$$\%C = E * \frac{[A - (R * B)]}{10} * W$$

Where,

R = Concentration ratio between potassium dichromate and ferrous ammonium sulfate.

A1 = Volume of potassium dichromate solution in blank sample, mL.

B1 = Volume of ferrous ammonium sulfate solution in blank sample, mL.

A2 = Volume of potassium dichromate solution in sugar solution sample, mL.

B2 = Volume of ferrous ammonium sulfate solution in sugar solution sample, mL.

A = Volume of potassium dichromate solution in soil sample, mL.

B = Volume of ferrous ammonium sulfate solution in soil sample, mL.

E = Carbon equivalent to potassium dichromate, mg C/mL.

D = Volume of standard sugar solution, mL.

0.842 = mg carbon per mL standard sugar solution.

W = Weight of sample, g.

CLEANUP

- Dispose any hazardous waste from flasks, burets, and beakers, in accordance with all local, state, and federal regulations, into respective waste containers

- Rinse and clean area of operation with water.

- Clean glassware thoroughly after each test with water and soap.

STORAGE

- Store all chemicals into tightly closed containers in a dry, cool, and well-ventilated area.

- Do not store potassium dichromate near combustible materials.

- Never allow sodium fluoride to get in contact with water during storage, and do not store near acids.