



The Applicability of a Field pH Meter in a Laboratory Setting

Evaluation of Field pH Meter in Compost and Soil Monitoring as a Resource-Efficient Alternative to Standardised Methodology

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BACHELOR'S THESIS
June 2022

Degree Programme in Energy and Environmental Engineering

ABSTRACT

Tampereen ammattikorkeakoulu
Tampere University of Applied Sciences
Degree Programme in Energy and Environmental Engineering

BARTUSEVICS, FINNJA:

The Applicability of a Field pH Meter in a Laboratory Setting. Evaluation of Field pH Meter in Compost and Soil Monitoring as a Resource-Efficient Alternative to Standardised Methodology

Bachelor's thesis 53 pages, appendices 6 pages
June 2022

The aim was to identify if a field pH meter can be used in monitoring soil and compost pH as a more time-efficient but as accurate method compared to the standardised method described in EN 13037:2011. The study was commissioned by the Environmental Laboratory Department at Tampere University of Applied Sciences.

This was done by conducting a comparative assessment using quantitative and qualitative methods. The quantitative research included a series of analyses on four (4) samples with varying acidities, from about pH 4 to 9, of which four (4) replicas were produced and measured with two (2) types of field pH meters; the pen tester HI981030 and the handheld meter HI98168, both from Hanna Instruments, using direct sample measurements and comparing these to the values obtained with the benchtop meter FEP20 from Mettler Toledo applying standard method EN 13037:2011 using un-dried and dried samples. Recorded values were used to determine the average pH and temperature. Each method was timed, from meter calibration through sample measurement and cleaning. The qualitative part consisted of observations made during device handling to evaluate device characteristics and establish the lack of features needed in a laboratory-scale meter.

The findings revealed differences in direct and standard measurements. The pH values acquired with both methods were comparable within the first unit. However, the values obtained with field meters were more comparable due to agreement within the first unit, and the mantissa's figures were adjacent to some degree, with a difference of 0.12 to 0.23 pH units; this also applied to the readings obtained with the FEP20 benchtop meter with un-dried and dried samples, which varied between 0.04 to 0.54 pH units. The direct measuring approach, including calibration, was shown to take about 65 minutes to 70 minutes, and the standard method with dried samples 5 hours and 55 minutes, and un-dried samples 4 hours and 55 minutes.

None of the meters seemed to be preferable to the others. Pen tester HI981030 was considered unsuitable for laboratory usage due to insufficient sample temperature and calibration efficiency information. From the perspective of time efficiency, field pH meters might be utilised for monitoring. Since there was a variance in pH values, it would be desirable to conduct similar research to determine the cause.

Key words: compost, pH meter, monitor, pH, soil, field pH meter

TIIVISTELMÄ

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Kesäkuu 2022

Tämä tutkimus toteutettiin Tampereen ammattikorkeakoulun ympäristölaboratorion toimeksiannosta, tavoitteena oli arvioida, täydentävää tapaa monitoroida kompostin ja maaperän pH:ta käyttäen kenttämittaria ja selvittää, voisiko se osoittautua aikatehokkaammaksi mutta yhtä tarkaksi menetelmäksi kuin eurooppalaisessa standardissa (EN) 13037:2011 määritetty menetelmä.

Tutkimuksessa käytettiin vertailevaa lähestymistapaa, johon sisältyi määrällisiä ja laadullisia menetelmiä. Määrälliseen analyysiin kuului neljän (4) näytteen mittaussarja, joiden happamuus oli noin pH 4:n ja 9:n välillä. Kustakin näytteestä otettiin neljä (4) rinnakkaista näytettä, joiden mittausarvoja käytettiin keskimääräisen pH:n ja lämpötilan määrittämiseen. Vertailussa käytettiin kahta erityyppistä kenttäkäyttöön tarkoitettua pH-mittaria, kynämittari HI981030 ja käsikäyttöinen mittari HI98168, molemmat Hanna Instrument:ilta, joita verrattiin laboratoriopöytämittariin FEP20 Mettler Toledo:lta. Kenttämittareiden kanssa käytettiin näytteen suoraa mittausmenetelmää ja pöytämittarilla käytettiin EN 13037:2011:ssä määriteltä menetelmää käyttämällä kuivattuja ja kuivaamattomia näytteitä. Mittausmenetelmä, mukaan lukien mittarin kalibrointi, näytteen valmistus, näytteen mittaaminen ja siivous, ajoitettiin alusta loppuun. Tutkimuksen laadullinen osa koostui laitteen käsittelyn aikana tehdyistä havainnoista, joilla arvioitiin laitteen ominaisuuksia, jotta voitiin todeta puuttuvat ominaisuudet, joita laboratoriomittarissa tarvitaan.

Molemmilla menetelmillä mitatut pH-arvot olivat vertailukelpoisia ensimmäisen yksikön rajoissa. Kuitenkin kenttämittareilla mitatut arvot olivat vertailukelpoisempia keskenään, sillä ne olivat yhdenmukaisia ensimmäisen yksikön tarkkuudella ja desimaaliosan luvut olivat jossain määrin lähellä toisiaan, ero oli 0.12 - 0.23 pH-yksikköä, tämä koski myös pH-arvoja, jotka mitattiin laboratoriopöytämittarilla FEP20 kuivatuilla ja kuivaamattomilla näytteillä, ero oli 0.04 - 0.54 pH-yksikköä. Suoran mittausmenetelmän todettiin kestävän noin 65 minuutista 70 minuuttiin, kun taas standardimenetelmä kuivatuilla näytteillä kesti 5 tuntia ja 55 minuuttia ja kuivaamattomilla näytteillä 4 tuntia ja 55 minuuttia.

Mikään mittari ei osoittautunut olevan muita parempi. Laitteen ominaisuuksien osalta kävi kuitenkin ilmi, että kynämittari HI981030 ei sovellu laboratoriokäyttöön, koska se ei ilmoita kalibrointitehokkuutta ja lämpötilaa. Suora mittausmenetelmä on osoittautunut aikatehokkaaksi, mutta pH-arvojen erojen vuoksi ei voitu todeta, olivatko molemmat menetelmät yhtä tarkkoja, ja siksi on tarvetta aiheen jatkotutkimukseen.

Asiasanat: Komposti, pH-mittari, monitorointi, pH, maaperä, kenttä-pH-mittari

CONTENTS

1	INTRODUCTION	7
2	THEORY	8
2.1	pH	8
2.2	Temperature Dependence of pH.....	8
2.3	Working Principle of a pH Meter.....	9
2.4	Anatomy and Function of a pH Probe	10
2.5	pH Probe Key Elements.....	11
2.5.1	pH Probe Shaft Material	11
2.5.2	Electrode	12
2.5.3	Glass Membrane Properties and Tip Shape.....	12
2.5.4	Junction Design.....	13
2.5.5	Fill Types and Reference Electrolyte	14
2.5.6	Junction Type	15
2.6	Calibration and Operation	16
2.7	Fundamentals of pH Measuring Practises	17
2.8	pH Meters	17
2.8.1	Fundamentals of pH Meter Parameter Specifications	18
2.9	The Experimental Instruments	18
2.9.1	Hanna Instruments HI981030 pH Pen Tester.....	18
2.9.2	Hanna Instruments HI98168 Handheld pH Meter.....	19
2.9.3	Mettler Toledo FEP20 Benchtop pH Meter.....	20
2.10	Test Substrates	21
2.10.1	Compost.....	21
2.10.2	Soil	22
2.11	EN 13037:2011 Standard	22
3	MATERIAL AND METHODS	23
3.1	Preparation and Collection of Test Substrate.....	23
3.1.1	Compost Preparation.....	24
3.1.2	Soil Sample Collection.....	25
3.2	Determination of pH with Field pH Meters.....	26
3.2.1	Calibration of Field pH Meters	26
3.2.2	Direct Soil pH Measurement.....	26
3.3	Standard Procedure with Benchtop pH Meter FEP20	28
3.3.1	Preparation of Un-dried Samples	28

3.3.2	Preparation of Dried Samples.....	28
3.3.3	Calibration of FEP20 Benchtop Meter	29
3.3.4	pH Testing of Suspension with Un-dried Sample	29
3.3.5	pH Testing of Suspension with Dried Sample	30
3.4	Data Analysis	30
4	RESULTS	31
4.1	pH	31
4.1.1	pH Measurement in a Suspension.....	31
4.1.2	Direct Soil pH Measurement.....	32
4.2	Time Utilisation for Calibration	32
4.3	Time Utilisation for pH Measuring	33
4.3.1	Suspension with Un-dried Sample.....	33
4.3.2	Suspension with Dried Sample.....	34
4.3.3	Direct Soil Measurement	35
4.4	Observation of Device Operation Characteristics.....	35
4.4.1	HI981030 Pen Tester	36
4.4.2	HI98168 Handheld pH Meter	36
4.4.3	FEP20 Benchtop pH Meter.....	36
5	DISCUSSION	38
5.1	Analysis of pH measurements and Time Utilisation	38
5.2	Analysis of Device Characteristics	41
6	CONCLUSION	43
	REFERENCES	45
	APPENDICES.....	49
	Appendix 1. Un-dried sample mass	49
	Appendix 2. Dried sample mass	50
	Appendix 3. Un-dried sample pH measurements	51
	Appendix 4. Dried sample pH measurements.....	52
	Appendix 5. Direct soil pH measurements	53
	Appendix 6. Calibration time	54

GLOSSARY

ATC	Automatic temperature compensation
EN	European Standard
H ⁺	Hydrogen ion
KCl	Potassium chloride
MTC	Manual temperature compensation
OH ⁻	Hydroxide ion
SD	Standard deviation
TAMK	Tampere University of Applied Sciences
μ	Mean
σ	Standard deviation

1 INTRODUCTION

Monitoring soil and compost pH is a common task in a life science laboratory and can be complex and resource-intensive if a standardised methodology is applied. Therefore, the Environmental Laboratory Department at Tampere University of Applied Sciences (TAMK) has commissioned this thesis research project to evaluate a supplementary way of monitoring soil and compost pH using a field pH meter.

The aim is to determine whether a field pH meter can be used in pH monitoring as a more sustainable and time-effective but as accurate measurement method compared to standard laboratory methods specified by the European Committee for Standardization, such as the European Standard (EN) 13037:2011, which specifies an instrumental method for determining pH in a suspension of soil improvers or growing media (SFS 13037 2011, 4). Therefore, a series of analyses will be carried out in June 2021 in the laboratory facilities of TAMK to recognise the potential of a field pH meter in a laboratory environment. Two (2) types of field pH meters, the pen tester HI981030 and the handheld meter HI98168, both from Hanna Instruments, following the manufacturer's specified method of direct soil pH measurement, will be compared to the standard laboratory benchtop pH meter FEP20 from Mettler Toledo, applying the methodology of EN 13037:2011.

The sample setup will consist of four (4) samples with varying acidity levels to create a pH scale that will range from acidic to alkaline. Each sample will be subjected to four (4) repeat measurements to determine the average and consistency of the results. Every step is methodically timed from beginning to end throughout the procedure, including equipment calibration, sample preparation, and sample measurement. Furthermore, the usage features, technical differences, and probe design are examined in order to conclude the feasibility of a field pH meter in soil and compost pH monitoring applications.

2 THEORY

2.1 pH

The pH value describes the hydrogen ion (H^+) concentration, or more precisely, the activity of H^+ in a substance whose solvent is water. pH is the negative logarithm of the H^+ concentration in moles per litre (mol/L). The pH/ H^+ formula (1) describing this relationship is as follows,

$$pH = -\log_{10} H^+ \quad (1)$$

where H^+ denotes the molar H^+ concentration.

In other words, it is a quantitative measure that describes the relative acidity or alkalinity of an aqueous substance. It is a number on a scale that in general ranges from 0 to 14, with 7 being neutral (see Figure 1). The higher the concentration of H^+ , the lower the pH (below 7) and the higher the acidity. For alkalis, the opposite is true: the lower the concentration of H^+ , the higher the pH (above 7) and, subsequently, the higher its alkalinity. (Timberlake & Timberlake 2017, 490-492.)



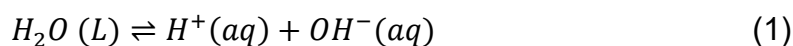
FIGURE 1. pH scale. Figure modified from Timberlake, K. & Timberlake, W. Basics Chemistry. Global edition, 2017, 491

2.2 Temperature Dependence of pH

Temperature plays a significant role in pH measurements. The relationship between temperature and pH can be explained by Le Châtelier's principle. According to the principle, when one of the factors that represent a system at

equilibrium, such as temperature, pressure, volume, or concentration, changes, the state of equilibrium shifts to compensate for the change. (Gaffney & Marley 2018, 529-532.)

For instance, when the temperature of an aqueous solution increases, the equilibrium will shift to decrease the temperature, leading to the absorption of additional heat - the shifting of the equilibrium results in the self-ionisation of water. As a result, the water molecules split into H^+ and hydroxide ions (OH^-). The following reaction scheme illustrates the chemical reaction of water autoionization into H^+ and OH^- (1)



when the temperature increases, the pH decreases and vice versa. (Westlab 2017.)

2.3 Working Principle of a pH Meter

A pH meter is a scientific instrument for chemical analysis used to measure the H^+ activity in an aqueous substance. A pH meter consists of a high input impedance meter and a pH probe containing an indicating and a reference electrode. It is a potentiometer that measures the electrical potential generated by H^+ between two electrodes. The principle of operation is based on Nernst's equation (2), which relates the electrical voltage to H^+ concentration,

$$E = \frac{R \times T}{n \times F} \times \log \frac{C_1}{C_2} \quad (2)$$

where variable E is the Nernst potential, equal to the potential difference in millivolts (mV). R denotes the molar gas constant ($8.31439 \text{ J} \times \text{mol}^{-1} \times \text{K}^{-1}$), and F denotes the Faraday constant ($96495.7^\circ\text{C} \times \text{mol}^{-1}$). n describes the ion charge and T the absolute temperature in Kelvin. C_1 indicates the ion concentration (mol/L) in the measured solution measured with the indicating electrode, and C_2

indicates the ion concentration (mol/L) in the reference cell. (Hamilton Company n.d.)

2.4 Anatomy and Function of a pH Probe

The main components of a combination pH probe are the electrode body, the measuring system (including glass membrane, indicating electrode and inner electrolyte), and the reference system (including reference electrode, reference electrolyte, and junction), as seen in Figure 2. (Cushman 2019.)

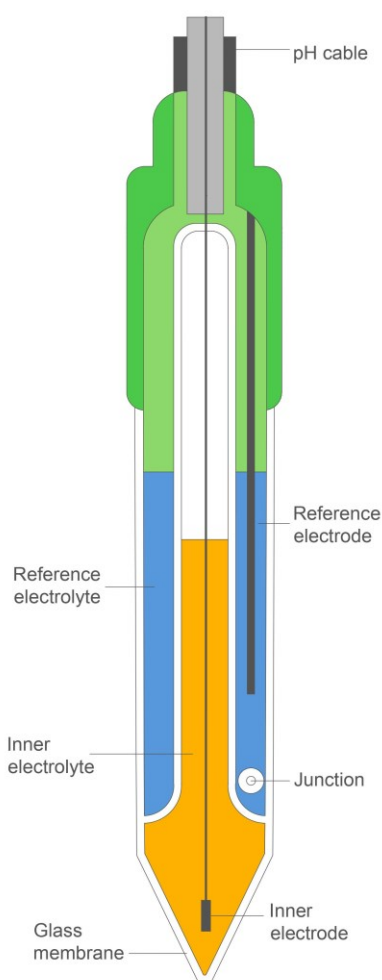


FIGURE 2. pH probe. Figure modified from Cushman C. Anatomy of pH Electrodes. 2019.

The probe body has a rod-like structure, and the end consists of an H^+ sensitive glass membrane that is permeable to H^+ and is sealed at the end to form a tip.

The inner sensing tube is filled with an inner electrolyte buffered at pH 7 with constant H^+ activity and an indicating electrode. The reference system is located outside the inner sensing tube in the reference chamber. The reference chamber contains a reference electrode immersed in a chemically neutral reference electrolyte (typically potassium chloride (KCl)). The reference electrolyte leaks from the junction, creating contact between the reference system and the sample to complete the circuit. It also protects the reference chamber from contaminants (see Figure 2). The pH value is calculated from the reference and measuring systems' potential differences. (Cushman 2019.)

When the pH probe is immersed into a sample, the H^+ in the sample penetrate the glass membrane's boundary area, and the indicating electrode is in contact with the inner electrolyte, which contains a constant H^+ activity. At the same time, the reference electrode is in contact with the reference electrolyte, which is subjected to the sample in which a changing amount of H^+ activity occurs through the reference junction. The difference in H^+ produces an output voltage that is measured and displayed as pH. (Cushman 2019.)

2.5 pH Probe Key Elements

2.5.1 pH Probe Shaft Material

The material of the probe's body depends on the application. Glass is resistant to various chemicals and has good thermal conductivity, making it ideal for general laboratory use when a fast response is required. Plastic, such as polyoxymethylene (POM) and polyvinylidene fluoride (PVDF), is used as a body material due to its chemical resistance and durability (SpecialChem n.d.; Hanna Instruments n.d., 2). Due to plastic's durability, it is often used on portable meters or anywhere that durability is required (Hanna Instruments n.d., 2).

2.5.2 Electrode

An electrode is a conductor that connects to the non-metallic circuit components of a circuit, such as an electrolyte (Corrosionpedia 2019). A pH probe possesses an indicating electrode and a reference electrode. These are essential to performing a potential measurement. The indicating electrode is one of the two electrodes in which the response changes according to the changes in the sample. The reference electrode is one of the two electrodes with a stable potential. The internal electrode is commonly a silver wire covered with silver chloride (Ag/AgCl), and the reference electrode is often the same material. (Sinbadlab 2021.)

2.5.3 Glass Membrane Properties and Tip Shape

The glass membrane can have different properties and shapes depending on the application of the probe. The selection is contingent on sample consistency, volume, temperature, the necessary measurement range, and ion activity. (Mettler Toledo 2016, 56.) Since ion exchange between the glass membrane and the sample is the foundation of measuring the potential difference, the formulation of the glass membrane is important for the measurement properties of the probe, determining electrode response. The membrane glass is a mixture of different metal oxides that function as a network, and the main component of the boundary layer, which acts as a network binder, is silicon dioxide. The membrane resistance is determined by its formulation and varies according to application and operating conditions. For measurements at low temperatures, a low-ohm membrane glass is used. In high-temperature applications, a membrane with a high impedance is used. (Schleicher n.d., 2.)

The two (2) most frequent membrane shapes are spherical and conical. A sphere-shaped tip provides a large contact area. This tip shape is ideal for measuring aqueous solutions, but it can be used for most applications. Because of its shape,

a conical tip is particularly well suited for measuring semi-solid media such as soil. (Hanna Instruments n.d.)

2.5.4 Junction Design

A pH probe's junction is the communication point between the reference electrolyte in the reference chamber and the sample. The reference electrolyte flows out into the sample in order for the probe to achieve accurate values. (Cole-Parmer 2018). In a single-junction probe, the junction is in direct contact with the sample, as seen in Figure 3.

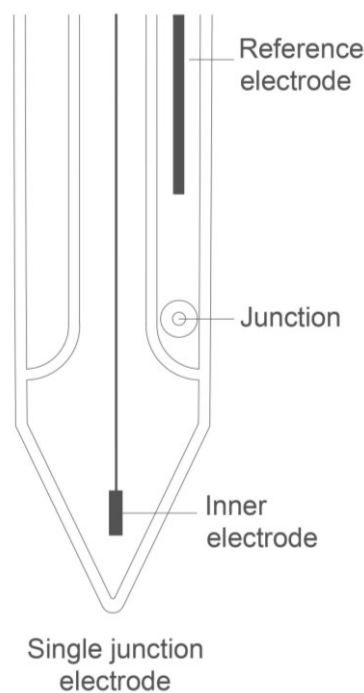


FIGURE 3. Single junction electrode structure. Figure modified from Hanna Instruments. n.d. Getting To Know Your pH Electrode, 1

Under unfavourable circumstances, such as high pressure, high temperature, or very acidic or alkaline conditions, the electrolyte flow may reverse, allowing samples to enter the reference chamber. The contaminants might react with the reference electrolyte or the reference electrode and, therefore, clog the junction, resulting in inconsistent readings or deterioration of the reference electrode. A pH electrode equipped with a single junction is inexpensive to manufacture but has a shorter life due to its compromised design. A single-junction probe is suitable

for general and cleaner water applications where the risk of sample ingress is reduced. (Bauman 2012.)

2.5.5 Fill Types and Reference Electrolyte

All pH probes have a reference electrolyte inside the reference chamber. This solution provides a stable reference potential to close the electrical circuit. The reference solution can be refillable or non-refillable. (Hanna Instruments n.d., 2.) A refillable pH probe is one in which the reference electrolyte can be refilled or replaced as needed. The frequency depends on the type of junction and its flow rate. This type of probe needs occasional maintenance. Non-refillable probes are filled with a gel electrolyte and do not require maintenance. As the electrolyte cannot be replaced in the case of contamination, the lifecycle can be shorter. (Sensorex 2016; Hach 2021.)

A reference electrolyte must have specific properties. Since the electrolyte leaks into the sample, it must be chemically neutral in order not to cause a reaction. In addition, the ions in the electrolyte must be equally mobile for good electrical conductivity. KCl possesses all of these characteristics. Therefore, KCl is the most commonly used reference electrolyte. (Cushman 2019.)

The two (2) most common types of reference electrolytes are liquid and gel. Liquid electrolytes are typically used in refillable pH probes. It also possesses a faster response time and has fewer limitations in the range of use than a gel electrolyte. A gel electrolyte consists of KCl; a thickening agent is added to make it more viscous to prevent it from freely leaking into the sample past the junction. A gel electrolyte is typically used in non-refillable probes and has lower resistance to temperature and temperature changes. (Cushman 2019.)

2.5.6 Junction Type

The flow rate of a junction must have specific properties, such as a large and consistent flow rate (in microliters per hour ($\mu\text{L/h}$)), to produce a stable reference potential and, therefore, precise measurements. The junction must only be slightly permeable; the permeability depends on the junction type. In addition to permeability, the material must have low electrical resistance and be chemically stable. (Cushman 2019.) Any blockage of the junction will result in unreliable and unstable measurements (Hanna Instruments, n.d., 1.)

The most frequent junction type is the ceramic junction. It is a porous ceramic component that is placed into the probe's shaft. The junction properties allow the electrolyte to flow slowly out of the probe. (Mettler Toledo 2016, 48.) Ceramic junctions have an outflow rate of 15 to 20 $\mu\text{L/h}$ and a high electrical resistance of one (1) kilohm ($\text{k}\Omega$) (Cushman 2019; Hanna Instruments n.d.). However, due to the porous structure of the ceramic, it is prone to clogging, particularly when measuring a viscous sample or suspension (Mettler Toledo 2016, 49).

Another type of junction is the open junction. In an open junction electrode, the reference electrolyte is in direct contact with the sample solution. This type of junction is only possible with a solid interface. The advantage of this type of junction is that it can hardly clog. It also has a high flow rate, ideal for semi-solids. (Mettler Toledo 2016, 51.)

Another common junction is the fibre or cloth junction, which is commonly used with probes that have a plastic shaft and a gel interface (Cushman 2019). In this type of junction, the reference opening is plugged with a plastic fibre pin. This type of junction is renewable because it can be pulled out to expose a fresh surface. (Hanna Instruments n.d.,14.)

2.6 Calibration and Operation

When it comes to pH measurement, calibration is a necessary step to obtaining accurate and reliable pH readings. The importance of calibration can be explained by the Nernst equation. The Nernst equation connects a voltage (mV) measurement to an ion concentration. A straight line represents this connection. The anticipated offset mV value at pH 7.0 in a temperature range of 25°C is 0 mV, and the slope of the line is 59.16 mV. This indicates that the electrode's output varies by 59.16 mV for each pH unit. (Gschwind 2020.)

The true offset is determined by measuring the mV output in a pH 7.0 buffer, and the slope (given in %) is calculated from (3),

$$\% \text{ slope} = \frac{(\Delta mV / \Delta pH \text{ units})}{(59.16 mV / pH \text{ units})} \times 100 \quad (3)$$

where ΔmV is the absolute potential difference between the buffers, ΔpH is the difference in pH units between the buffers. $59.16 mV / pH \text{ units}$ represents the theoretical slope at 25°C. (Hanna Instruments n.d.)

Since the working principle of a pH probe is based on the Nernst equation, which incorporates absolute temperature, the slope is likewise temperature dependent. Because temperature affects the accuracy of pH measurements, pH probes typically include a temperature sensor to indicate the sample's temperature. Aside from the temperature sensor, the probes are equipped with temperature compensation, which is either automatic temperature compensation (ATC) or manual temperature compensation (MTC). (Cole-Parmer 2018.) During the calibration process, the ATC unit measures and logs the temperature of the buffer. Then, when the sample is measured, the ATC constantly measures its temperature and adjusts the pH values to match the calibrated value. (Bluelab n.d.) MTC requires the user to input the sample temperature manually. (Cole-Parmer 2018).

2.7 Fundamentals of pH Measuring Practises

The slope and offset will change as the electrode ages. Therefore, to reduce errors and obtain reliable pH measurements, the pH meter should be calibrated with traceable buffers that bracket the expected pH of the samples, following the manufacturer's instructions. (Gschwind 2020; Hanna Instruments 2016; Inorganic Ventures n.d.) In addition, the pH meter should be calibrated at a similar temperature to that at which the sample is measured. Also, if pH measurements are to be compared, the samples should be at similar temperatures for coherent pH values. (Gschwind 2020.) The slope of a functional probe should be between 85% and 105%, and an offset of ± 30 mV is acceptable (Hanna Instruments 2016).

2.8 pH Meters

pH measurement is used in a broad range of applications, from home garden soil testing to environmental studies. Because of the wide range of applications for pH measurements, various types of meters are available. pH meters are classified into pen testers, handheld meters, and benchtop meters. (Instrumentchoice 2020.)

Pen testers are compact, pocket-sized instruments with an integrated display and electrode. Handheld meters are larger than pen testers and more rugged. In this type of meter, the electrode is built separately from the metre and can be interchanged depending on the pH measurement requirements. Handheld metres are designed for use in the field. Benchtop pH metres can be placed on a surface or mounted on a wall and are typically used in laboratories. (Instrumentchoice 2020.)

2.8.1 Fundamentals of pH Meter Parameter Specifications

A meter's or probe's range is the distance between the lowest and greatest value it can measure. Resolution describes the range of meters within which a signal can be read. The meter accuracy describes the discrepancy between the indicated and actual values. (Instrumentation-Electronics 2011.)

2.9 The Experimental Instruments

2.9.1 Hanna Instruments HI981030 pH Pen Tester

The HI981030 pH pen tester from Hanna Instruments is intended for direct pH measurements taken in soils and slurries. The tester includes a single button for operation and a liquid crystal display (LCD). It features a lithium-ion battery that can be replaced and has an operational duration of approximately 800 hours (h). The probe housing is made of polyvinylidene fluoride (PVDF). PVDF is a durable thermoplastic that is resistant to a wide range of chemicals and solvents. It possesses resistance to abrasion, mechanical strength, and resistance to ultraviolet light. (Hanna Instruments n.d.) Further technical specifications are shown in Table 1, which contains information on the testers' range, accuracy, calibration, operation limitations, and physical characteristics.

TABLE 1. HI981030 GroLine Soil pH Tester specification. Table was modified from Hanna Instruments. GroLine Soil pH Tester, n.d.

Specifications	
Range	0.00 to 12.00 pH
Resolution	0.01 pH
Accuracy (at 25°C)	± 0.05 pH
Calibration	Automatic, one or two-point
Temperature compensation	ATC, 0 to 50°C
Environment	0 to 50°C
Dimensions	51 x 151 x 21 mm
Weight	46 g

The pH probe is integrated into the housing and cannot be replaced. The tip of the electrode has a conical shape, which is ideal for semi-solid substances. The probe features a refillable open junction with a gel interface and a removable PVDF reference sleeve. (Hanna Instruments n.d.)

2.9.2 Hanna Instruments HI98168 Handheld pH Meter

Hanna Instruments' HI98168 handheld meter is a portable pH and temperature meter designed for field use and specifically engineered for direct soil measurements. The meter has a large LCD and a keypad for operation. It has an ingress protection (IP) rating of 67. (Hanna Instruments n.d.). According to the IP67 rating, the device is dust-tight and protected against the effects of temporary immersion in water (IEC n.d.). The device uses four (4) replaceable, 1.5-volt AA batteries for approximately 200 h of operation. Other capabilities such as log-on-demand enable the storage of up to 100 measurements, including date, time, calibration buffers, offset, and slope information. All logged measurements can be transferred to a computer via a USB port. (Hanna Instruments n.d.)

The pH and temperature probe (HI12923) is a refillable single-junction probe that connects to the meter via a Quick DIN connector. The electrode body is made of chemically resistant glass that quickly reaches thermal equilibrium. The probe's membrane glass has a conical shape and is made of low-temperature glass with a low resistance of approximately 50 megaohms (M Ω). The probe's reference system features an Ag/AgCl electrode and three (3) ceramic junctions, which improve the performance in soils with low moisture content. The ceramic junctions allow the electrolyte to flow out of the junction at 40 to 50 μ L/h. (Hanna Instruments n.d.). Technical specifications regarding the meters' and probes' range, precision, and calibration can be seen in Table 2.

TABLE 2. HI98168 pH meter and probe HI12923 specifications. Table was modified from Hanna Instruments. n.d. GroLine Professional Portable Soil pH Meter and Hanna Instruments. n.d. pH Electrode for Direct Soil Measurement

Specifications	
Range (Meter)	-2.00 to 20.00 pH
Range (Probe)	0.00 to 12.00 pH
Operating temperature (Probe)	-5 to 70°C
Resolution	0.1 pH / 0.01 pH / 0.001 pH
Accuracy	±0.1 pH / ±0.01 pH / ±0.001 pH
Calibration	Up to five-point calibration
mV Range	±2000.0 mV
mV Resolution	0.1 mV
mV Accuracy	±0.02 mV
Temperature compensation	ATC or MTC
Temperature range	-20.0 to 120.0°C
Temperature resolution	0.1°C
Temperature accuracy (at 25°C)	± 0.4°C
Environment	0 to 50°C
Dimensions	185 x 93 x 35.2 mm
Weight	400 g

2.9.3 Mettler Toledo FEP20 Benchtop pH Meter

Mettler Toledo's FEP20 benchtop meter has a large LCD and a thermoplastic (polycarbonate and acrylonitrile butadiene styrene) reinforced housing. It has five buttons to navigate through the system and operate the meter. An alternating current (AC) power plug powers the meter. Up to 99 endpoint measurements can be stored and, if required, printed out via a laboratory printer using an RS-232 interface. In addition, it is compatible with several types of probes. (Thermo Fisher Scientific n.d.)

The pH probe (LE438) with an integrated temperature sensor is connected to the meter via a one-meter cable with BNC/RCS connectors held by a probe holder arm. The probe shaft is made of POM, a thermoplastic material. The probe's tip is spherical, and the membrane glass is made of universal glass and has a resistance of 250 MΩ. The reference system is non-refillable and has a single-junction design, with a porous polyester plastic fibre junction, an Ag/AgCl electrode, and a gel electrolyte interface. The probe is intended for measuring the

pH of aqueous solutions with temperature fluctuations. (Mettler Toledo n.d.) In Table 3, additional technical data is reported.

TABLE 3. Mettler Toledo FEP20 pH Meter specifications. Table was modified from Thermo Fisher Scientific. n.d. Mettler Toledo FiveEasy Plus FEP20 pH Meter and Mettler Toledo. n.d. pH electrode LE438.

Specifications	
Range (Meter)	0.00 to 14.00 pH
Range (Probe)	0.00 to 14.00 pH
Operating temperature (Probe)	0 to 100°C
Resolution	0.01 pH
Accuracy	±0.01 pH
Calibration	Three-point
mV Range	-1999 to 1999 mV
mV Resolution	1 mV
Temperature compensation	ATC or MTC
Temperature range (Meter)	0 to 100°C
Temperature range (Probe)	0 to 80°C
Temperature resolution	0.1°C
Dimensions (Width)	175 mm
Weight	600 g

2.10 Test Substrates

2.10.1 Compost

Compost is obtained by biodegrading a mixture of organic matter in aerobic conditions. EN 14806:2005 specifies a methodology to prepare compost or synthetic solid waste under controlled conditions during a period of 45 days. The composting of the synthetic solid waste takes place in an environment where temperature, aeration, pH, and humidity are monitored. During the composting process, the pH of the matter shifts from acidic (about 6) to basic (about 8 to 9) during the first 10 to 15 days, becoming neutral-basic (about 7 to 8) at the end. (SFS 14806 2006, 5, 8-9.)

2.10.2 Soil

Soil forms from the gradual breakdown of rocks (parent material) through weathering. The process of weathering can be physical, chemical, or biological. (Buol, Southard, Graham, & McDaniel 2011, 141). The pH of natural soil is determined by the parent material and the weathering processes that occurred during its formation (The State of Queensland 2013). The soil pH influences the amount of soluble nutrients in the soil's water and, therefore, the plant's access to nutrients. Certain nutrients are more available in acidic environments, while others are more available in alkaline environments. Plant species are adapted to different pH ranges, and therefore, the predominant flora can serve as an indicator for soil pH. (Nutrientstewardship n.d.) For example, the predominant flora in mesic heath forests, in which the tree layer can consist of a mix of pine (*Pinus sylvestris*), spruce (*Picea abies*) and different broad-leaved trees, a field layer of subshrubs such as bilberry (*Vaccinium myrtillus*) and twinflower (*Linnaea borealis*), and a lower layer of different kinds of moss species such as feather mosses (*Ptilium crista-castrensis*), glittering wood moss (*Hylocomium splendens*) and fork mosses (*Dicranum*), has an average soil pH of about 4.0. (Suomen ympäristökeskus 2019.)

2.11 EN 13037:2011 Standard

The European Standard specifies an instrumental technique for determining the pH of a soil amendment. According to the standard, the sample shall be extracted with laboratory-scale water at $22 \pm 3.0^\circ\text{C}$ in a ratio of 1:5, one (1) part sample and five (5) parts water (SFS 13037 2011, 4). The sample for extraction shall be prepared per EN 13040:2007 (SFS 13037 2011, 5). EN 13040:2007 specifies a procedure for preparing un-dried and dried samples (SFS 13040 2008, 5, 7). Furthermore, the pH meter shall be adjusted according to the manufacturer's instructions, and the buffers and samples' temperatures shall not differ by more than 1°C . The measurement shall be taken in a settling suspension, and values noted shall be expressed to the nearest 0.1 pH unit. (SFS 13037 2011, 6.)

3 MATERIAL AND METHODS

A comparative analysis was used to evaluate the feasibility of a field pH meter in compost and soil monitoring as a more sustainable and time-effective method compared to the standard method defined by EN 13037:2011. The evaluation was approached by conducting a literature review and using quantitative and qualitative research methods. The literature review was based on established research from books, scholarly articles, manuals, and information provided by pH meter manufacturers. Quantitative methods included laboratory analysis and the timing of each step. The qualitative approach involved the recording of observations during device handling.

The pH meters to be compared were the HI981030 pen tester, the HI98168 handheld meter from Hanna Instruments, and the FEP20 benchtop meter from Mettler Toledo. In order to minimise errors due to unfamiliarity with the field devices and measuring methods, a test round was performed prior to the true measurements, which were taken in June 2021.

The samples for the final analysis were determined during the test round. Several compost samples with varying maturity and soil samples from different sites were available for analysis, of which four (4) were selected for final analysis. Each sample was subjected to four (4) measurements to determine the measured values' average and range.

3.1. Preparation and Collection of Test Substrate

The sample setup included four (4) samples with varying acidities from pH four (4) to nine (9) which were determined during the test round. To ease recognition, the samples are named after alphabetical letters from A to D. Specimens A, B, and C, are compost samples prepared according to EN 14806:2005 with a pH

range from around six (6) to nine (9). Specimen D is a soil sample from a mesic heath type forest and has a pH of about four (4).

3.1.1 Compost Preparation

Compost sample preparation followed the guidelines of EN 14806:2005. The preparation was as follows: the components listed in Table 4 were manually mixed in a big plastic container and then the water content was adjusted to about 55%.

TABLE 4. Composition of compost. The table was modified from SFS EN 14806 2006, 6

Material	Dry mass %
Sawdust	40
Rabbit-feed	30
Compost	10
Starch	10
Sugar	4
Canola oil	4
Urea	2
Total	100

The compost mass was placed in composting reactor boxes and then into an oven with air circulation that maintained a constant temperature according to the specified temperature profile. The samples were treated throughout the composting process according to the treatment example given in EN 14806:2005.

3.1.2 Soil Sample Collection

Soil sample D was taken from the Kauppi Sports Park in Tampere, Finland (61°30'57" N, 23°48'31" E). The forest type in Kauppi Sports Park is a mesic heath forest. The soil was collected from a site where the vegetation consisted of bilberry, pine, and spruce (see Picture 3).



PICTURE 3. Vegetation at the soil sampling site (Author 2021)

Prior to sample collection, the vegetation was removed. Then, a hole of approximately 25 centimetres (cm) in depth was dug, and the soil was thoroughly mixed in the hole. Finally, the soil sample was collected into a 5-litre (L) non

transparent plastic bucket with a lid and taken to the Environmental Laboratory of TAMK for analysis.

3.2. Determination of pH with Field pH Meters

3.2.1 Calibration of Field pH Meters

The pH HI981030 pen tester and HI98168 handheld pH meter were calibrated prior to taking measurements according to the manufacturers' Hanna Instruments instructions. Two (2) standard buffer solutions at pH 4 and 7 were used for calibration. The effectiveness of the calibration for meter HI98168 can be seen in Table 6, which shows the final pH, slope, offset and calibration temperature.

TABLE 6. Calibration effectiveness pH meter HI98168

Calibration information pH meter HI98168	
Calibration 1 [pH]	4.01
Calibration 2 [pH]	7.01
Temperature 1 [°C]	21.5
Temperature 2 [°C]	21.5
Slope [%]	99.3
Offset [mV]	1

3.2.2 Direct Soil pH Measurement

Direct soil pH measurements were performed with the pen tester HI981030 and the handheld pH meter HI98168, both manufactured by Hanna Instruments. The method of direct soil measurement was given by the manufacturer and was identical for both devices.

Direct soil pH measurements were made on samples A, B, C, and D. The samples were transferred into a 2 L plastic container. Before the probe was inserted into the sample, the sample was perforated with a small auger to a depth of about 20

cm and, if necessary, moistened with a small amount of distilled water. The probe was then inserted into the perforated hole, and the measurement was observed until a stable reading was indicated (see Picture 4).



PICTURE 4. Direct soil pH measurement, top right HI981030 and bottom left HI98168 (Author 2021)

The measurement procedure was repeated four (4) times, and the probe was inserted at the same depth for each measurement. Before proceeding to measure the subsequent sample, the electrode was cleaned with tap water, and all residues were carefully removed.

3.3. Standard Procedure with Benchtop pH Meter FEP20

All four (4) samples, A, B, C, and D, were divided and prepared for pH determination according to EN 13040:2007 un-dried and dried sample preparation instructions. The determination of pH in compost samples A, B, and C and soil sample D followed the guidelines of EN 13037:2011. Each sample suspension pH measurement was done with Mettler Toledo's FEP20 benchtop pH meter. The pH meter was calibrated prior to taking measurements according to the manufacturer's Mettler Toledo instructions.

3.3.1 Preparation of Un-dried Samples

The un-dried samples were thoroughly mixed, and any lumps were carefully broken to obtain a homogenous material. Approximately 30 millilitres (mL) of each sample were weighed, and this procedure was repeated four (4) times to ascertain the average weight of the 30 mL sample. This was done for each of the four (4) A, B, C, and D samples. The average mass in grammes (g) of 30 mL of the un-dried sample is given in Appendix 1.

3.3.2 Preparation of Dried Samples

A section of the test materials was dried at room temperature at approximately 21°C on aluminium trays under a fume extractor until they crumbled to the touch and then ground using a grinder. The average mass of 25 mL was determined and replicated four (4) times to establish the average mass of a 25 mL sample. This was repeated on all four (4) A, B, C, and D samples. The values for the average mass in g of a 25 mL dried sample can be found in Appendix 2.

3.3.3 Calibration of FEP20 Benchtop Meter

The Benchtop pH meter FEP20 was calibrated as prescribed in the manufacturer's Mettler Toledo manual, using two traceable buffer solutions at pH 4 and 7. The effectiveness of the calibration is reported in Table 5 below, which shows the slope and offset of the calibration, including the calibration temperature.

TABLE 5. Calibration effectiveness pH meter FEP20

Calibration information pH meter FEP20	
Calibration 1 [pH]	4.01
Calibration 2 [pH]	7.01
Temperature 1 [°C]	22.5
Temperature 2 [°C]	22.5
Slope [%]	98
Offset [mV]	1

3.3.4 pH Testing of Suspension with Un-dried Sample

Four (4) replicas were produced from samples A, B, C, and D to determine the pH of a suspension with an un-dried sample using the benchtop pH meter FEP20. Each sample was extracted with deionised water (grade 2, conductivity of $<1\mu\text{S/cm}$) for analytical laboratory use at a 1:5 (30 mL un-dried sample + 150 mL water) excitation ratio in a glass beaker. The sample suspension was mixed with a magnetic stirrer for 1 h. The suspension was allowed to settle for 1 h and 30 minutes (min). Immediately before measurements, the suspension was agitated thoroughly. Next, the pH and temperature were taken while the suspension was settling until the meter indicated stable readings. The probe was rinsed with deionised water to remove any sample residue between measurements. Detailed information on the sample volume in mass used for each un-dried sample replicate can be found in Appendix 1.

3.3.5 pH Testing of Suspension with Dried Sample

To determine the pH of a suspension with a dried sample using the benchtop pH meter FEP20, four (4) replicas were produced from samples A, B, C, and D. Each sample was extracted with deionised water (grade 2, conductivity of $<1\mu\text{S}/\text{cm}$) at an excitation ratio of 1:5 (25 mL of dried sample and 125 mL of water). The suspension of the dried sample and water was mixed for 1 h with a magnetic stirrer. The mixture was allowed to settle for 1 h and 30 min. The suspension was extensively mixed prior to measurement, and pH and temperature were measured in the settling suspension. Between measurements, the probe was rinsed with deionised water to eliminate any traces of the previous sample. Appendix 2 contains information that specifies the exact amount of sample used for each replica.

3.4 Data Analysis

After the measurements of pH, temperature and time utilisation were taken, the average of the measured values was calculated to estimate the true value and then used to compare averages to determine if there were significant differences between the values. In addition, repeatability was defined using standard deviation (SD (σ)), which expresses the variation of individual measurements around average values.

4 RESULTS

4.1 pH

4.1.1 pH Measurement in a Suspension

The average pH and temperature of four (4) replicas of samples A, B, C, and D were found by applying the method of EN 13037:2011 to un-dried and dried samples prepared according to EN 13040:2007 and measured with the FEP20 benchtop pH meter from Mettler Toledo. The results are shown in Table 7, in addition to SD, which presents the sample range.

As it can be seen, the average pH and temperature measured for dried samples A, B, C, and D were for sample A, 6.54 at 23.2°C; sample B, 7.83 at 22.9°C; sample C, 8.21 at 23.4°C; and sample D, 4.39 at 23.6°C. On the other hand, the average pH for un-dried specimens A, B, C, and D was the following: sample A, 6.83 at 23.4°C; sample B, 8.07 at 22.8°C; sample C, 8.75 at 23.0°C; and sample D, 4.43 at 22.9°C. The individual measurements for un-dried samples are reported in Appendix 3 and dried samples in Appendix 4.

TABLE 7. Average pH and temperature values measured with the FEP20 pH meter

Sample	Average pH of dried sample ($\mu \pm \sigma$, n= 4)	Average temperature [°C] of dried sample ($\mu \pm \sigma$, n= 4)	Average pH of un-dried sample ($\mu \pm \sigma$, n= 4)	Average temperature [°C] of un-dried sample ($\mu \pm \sigma$, n= 4)
A	6.54 \pm 0.01	23.2 \pm 0.1	6.83 \pm 0.05	23.4 \pm 0.3
B	7.83 \pm 0.00	22.9 \pm 0.1	8.07 \pm 0.03	22.8 \pm 0.1
C	8.21 \pm 0.02	23.4 \pm 0.4	8.75 \pm 0.03	23.0 \pm 0.2
D	4.39 \pm 0.01	23.6 \pm 0.2	4.43 \pm 0.04	22.9 \pm 0.1

4.1.2 Direct Soil pH Measurement

The average pH and temperature of four (4) replicas of samples A, B, C, and D were determined by applying the method of direct soil measurement measured with the HI981030 pen tester and the HI98168 handheld meter both from Hanna Instruments. The measured values and SD indicating the sample range are indicated in Table 8.

As indicated in the table below, the HI981030 pen tester registered an average pH of 5.94 for sample A, 7.39 for sample B, 8.86 for sample C, and 4.09 for sample D. The average pH and temperature measured with the HI98168 handheld meter were 5.82 at 21.9°C for sample A, 7.21 at 22.1°C for sample B, 8.69 at 22.3°C for sample C, and 4.32 at 21.7°C for sample D. The individual values of pH and temperature can be reviewed in Appendix 5.

TABLE 8. Average pH and temperature of direct soil measurements with HI98168 and HI981030

	Instrument		
	HI981030	HI98168	
Sample	Average pH ($\mu \pm \sigma$, n= 4)	Average temperature [°C] ($\mu \pm \sigma$, n=4)	
A	5.94 \pm 0.04	5.82 \pm 0.08	21.9 \pm 0.2
B	7.39 \pm 0.06	7.21 \pm 0.10	22.1 \pm 0.2
C	8.86 \pm 0.04	8.69 \pm 0.03	22.3 \pm 0.0
D	4.09 \pm 0.07	4.32 \pm 0.11	21.7 \pm 0.1

4.2 Time Utilisation for Calibration

Two-point calibration was performed four (4) times on the HI981030 pen tester, the HI98168 handheld meter, and the FEP20 benchtop meter. The time utilisation was methodically recorded, including preparation, calibration, and cleaning. The average time utilisation for each pH meter calibration can be seen in Table 9.

The average time to calibrate the HI981030 pen tester was about 17 min, 16 min for the HI98168 handheld meter, and 16 min for the FEP20 benchtop meter.

Overall, the calibration times varied from about 16 to 17 min. The individual time measurements are shown in Appendix 6.

TABLE 9. Average time for pH meter calibration

Instrument		
HI981030	HI98168	FEP20
Average calibration time [hh:min:ss] ($\mu \pm \sigma$, n = 4)		
00:16:49 \pm 00:02:43	00:15:37 \pm 00:03:03	00:16:22 \pm 00:01:23

4.3 Time Utilisation for pH Measuring

4.3.1 Suspension with Un-dried Sample

The time required to investigate the pH of un-dried samples A, B, C, and D, four (4) individual replicas utilising the method defined in EN 13037:2011, was measured and is displayed in Table 11 below. As shown in Table 11, the total time used was about 4 h 40 min. This can be broken down as follows: weighing the samples took 1 h, settling up the equipment took 15 min, mixing the samples took 1 h, letting the samples settle took 1 h and 45 min, measuring the pH took 20 min, and cleaning took 20 min.

TABLE 11. Time utilisation for slurry pH testing using un-dried sample

Procedure	Time utilisation [hh:min]
Weighing	01:00
Preparing setup	00:15
Mixing	01:00
Settling	01:45
pH measurement	00:20
Cleaning	00:20
Total time utilisation	04:40

4.3.2 Suspension with Dried Sample

The time required to measure the pH of samples A, B, C, and D and their four (4) replicas, using the approach described in EN 13037:2011 using dried samples and the FEP20 benchtop meter, was timed, and the results are provided in Table 10. As presented in Table 10, the total time utilisation was approximately 5 h and 40 min, which may be broken down as follows: sample grinding, 1 h; sample weighing, 1 h; preparation of the setup, 15 min; sample mixing, 1 h; sample settling, 1 h and 45 min; pH measurement, 20 min; and cleaning, 20 min.

TABLE 10. Time utilisation for slurry pH testing using dry sample

Procedure	Time utilisation [hh:min]
Grinding	01:00
Weighing	01:00
Preparing setup	00:15
Mixing	01:00
Settling	01:45
pH measurement	00:20
Cleaning	00:20
Total time utilisation	05:40

4.3.3 Direct Soil Measurement

The total time required for direct soil pH measurement with the HI981030 pen tester and the HI98168 handheld meter on samples A, B, C, and D, and repeating the measurement four (4) times, was measured. These values are presented in Table 12.

TABLE 12. Time utilisation for direct soil pH measurement with the HI981030 pen tester and the HI98168 handheld meter

Procedure	Time utilisation [hh:min]	
	Instrument	
	HI981030	HI98168
Preparing setup	00:15	00:15
pH measurement	00:30	00:20
Cleaning	00:15	00:15
Total time utilisation	01:00	00:50

Direct soil measurement with the HI981030 pen tester took 1 h. This can be broken down as follows: 15 min to prepare, 30 min to measure pH, and 15 min to clean. In comparison, the measurement with the HI98168 handheld meter took 50 min, of which 15 min were spent on preparation, 20 min on pH measurement and 15 on cleaning.

4.4 Observation of Device Operation Characteristics

While handling the HI981030 pen tester, the HI98168 handheld meter, and the FEP20 benchtop meter, their usability was observed and evaluated in terms of calibration, measuring procedures, and other features such as the probes' refill ability and interchangeability, to evaluate device characteristics and establish the lack of features needed in a laboratory-scale meter.

4.4.1 HI981030 Pen Tester

The pen-shaped HI981030 pH meter is compact and can be operated with one hand. The meter is characterised with one- or two-point calibration. During calibration, the meter automatically detects the buffer solution. In addition, the meter has ATC, but the temperature is not displayed. Furthermore, the calibration efficiency is not displayed. The probe reference system has a single junction design with a gel interface that can be cleaned and refilled if necessary. The probe is not replaceable since it is incorporated into the meter.

4.4.2 HI98168 Handheld pH Meter

During the HI98168 handheld pH meter calibration, the meter's probe must be constantly stirred in the buffer solution. The meter has ATC to compensate for changes in temperature and automatic buffer recognition, but the buffer values need to be selected a few times during calibration. After the reading has stabilised, the calibration point and temperature must be confirmed. When the calibration is completed, the calibration efficiency is displayed. The meter warns of possible problems during calibration, such as buffer contamination or issues with the probe. The pH calibration data is automatically saved after a successful calibration and can be recalled. The meter may be calibrated with up to five points. It is easy to navigate the meter's settings and revise stored data. The HI12923 probe reference system has a single junction design with a liquid interface and is refillable. The probe is quickly interchangeable. In addition, the pH meter is compatible with other types of probes.

4.4.3 FEP20 Benchtop pH Meter

The calibration of the FEP20 benchtop pH meter is relatively simple; when inserting the meter's probe into a buffer, the meter recognises it due to the incorporated automatic buffer recognition. After calibration, the effectiveness of

the calibration is displayed. The temperature and pH values are presented throughout the measurement, and when the parameters have stabilised, an icon is displayed on the screen to indicate the stabilised values. The meter may be calibrated with three (3) points. In addition, the meter has an ATC, which compensates for the temperature differences between the calibration temperature and the sample temperature. The measured data can be stored and reviewed at any time since the meter's menu is easy to navigate. Since the unit stands on a surface, the risk of damage to or spillage of the samples is significantly reduced. In addition, the probe holder arm minimises the risk of damage to the probe and simplifies measuring and calibrating as the probe does not need to be held, allowing hands-free measurement. The LE438 probe's reference system has a single junction design with a gel interface and is not refillable. In the event of contamination, the probe must be replaced, which can be done quickly due to the BNC/RCS connectors. In addition, the meter is compatible with other pH probes.

5 DISCUSSION

This section provides an assessment of the findings from the comparative analysis of the research conducted for TAMK to evaluate the feasibility of a direct soil field pH meter as a more resource-efficient method for pH monitoring of compost and soil in a laboratory environment compared to the method specified in EN 13037:2011, which provided relevant information.

In the evaluation, two (2) field pH meters intended for direct soil measurements, the HI981030 pen tester and the HI98168 handheld meter, both from Hanna Instruments, were compared to the FEP20 benchtop meter from Mettler Toledo using the standard method described in EN 13037:2011. Four (4) samples, A, B, C, and D, were tested in quadruplicate independently to establish the average and range of the measured results.

5.1 Analysis of pH measurements and Time Utilisation

For comparative purposes, the values obtained from measurements are collected in Table 13. The table below shows the calculated averages and range of pH, temperature, and time utilisation and the performed method. The range was defined by computing the standard deviation of a sample size that included four (4) samples. As for the pH values, they indicated similarities within the first digit. Conversely, the measurements obtained using the method of direct soil pH measurement with the HI981030 pen tester and the HI98168 handheld meter are more comparable since there is an agreement within the first unit and the mantissa's digits are adjacent to some extent, with a difference ranging from 0.12 to 0.23 pH units. The pH measurements recorded with the FEP20 benchtop meter using the EN 13037:2011 methodology with dried and un-dried samples differed from 0.04 to 0.54 pH units. The variance in reported pH values may be related to a number of factors, including calibration, temperature, measuring medium, methodology, probe characteristics and human resources constraints.

TABLE 13. Summary of Results

Instrument								
HI981030 Pen Tester (Hanna Instruments)		HI98168 Handheld Meter (Hanna Instruments)			FEP20 Benchtop Meter (Mettler Toledo)			
Meter Accuracy								
±0.05 pH		±0.01 pH / ± 0.04°C			±0.01 pH			
Calibration Efficiency								
-		Cal 1: 4.01 pH, Cal 2: 7.01 pH, Temp. 1: 21.5°C, Temp. 2: 21.5°C, slope: 99.3%, offset: 1 mV			Cal 1: 4.01 pH, Cal 2: 7.01 pH, Temp. 1: 22.5°C, Temp. 2: 22.5°C, slope: 98%, off-set: 1 mV			
Method								
Direct Soil Measurement					EN 13037:2011, Dried Sample		EN 13037:2011, Un-dried Sample	
Average pH ($\mu \pm \sigma$, n=4)		Average pH ($\mu \pm \sigma$, n=4)	Average Temperature [°C] ($\mu \pm \sigma$, n=4)	Average pH ($\mu \pm \sigma$, n=4)	Average Temperature [°C] ($\mu \pm \sigma$, n=4)	Average pH ($\mu \pm \sigma$, n=4)	Average Temperature [°C] ($\mu \pm \sigma$, n=4)	
Sample	A	5.94 ± 0.04	5.82 ± 0.08	21.9 ± 0.2	6.54 ± 0.01	23.2 ± 0.1	6.83 ± 0.05	23.4 ± 0.3
	B	7.39 ± 0.06	7.21 ± 0.10	22.1 ± 0.2	7.83 ± 0.00	22.9 ± 0.1	8.07 ± 0.03	22.8 ± 0.1
	C	8.86 ± 0.04	8.69 ± 0.03	22.3 ± 0.0	8.21 ± 0.02	23.4 ± 0.4	8.75 ± 0.03	23.0 ± 0.2
	D	4.09 ± 0.07	4.32 ± 0.11	21.7 ± 0.1	4.39 ± 0.01	23.6 ± 0.2	4.43 ± 0.04	22.9 ± 0.1
Method Time Utilisation [hh:min]		01:00	00:50		05:40		04:40	
Average Calibration Time Utilisation [hh:min:ss] ($\mu \pm \sigma$, n=4)		00:16:49 ± 00:02:43	00:15:37 ± 00:03:03		00:16:22 ± 00:01:23			

Validity is the most critical issue in pH measurement. To determine whether a pH meter gives an accurate measurement, it must be calibrated in standardised solutions. Based on the calibration efficiency, the measured values can then be validated. A meter is considered accurate when the probe slope is between 85% and 105% and the offset ± 30 mV (Hanna Instruments n.d.). Based on calibration efficiency, the values obtained with the HI981030 pen tester cannot be confirmed as the meter does not display calibration efficiency. The pH values obtained with the HI98168 handheld meter and the FEP20 benchtop meter can be confirmed as reliable. The slope of the HI98168 meter was 99.3% with an offset of 1 mV, and the slope of the FEP20 was 98.6% with an offset of 1 mV; both instruments were calibrated within the acceptable range.

The calibration buffers must also fall within the anticipated pH range of the samples to obtain reliable pH measurements (Geschwind 2020). However, the pH meters used for analysis were two-point calibrated with buffers of pH 4 and 7, which did not include the sample pH range of 4 to 9.

When measuring pH, two key factors to consider are calibration and sample temperature. This is due to the reliance of chemical reactions on temperature, which affects pH. Therefore, the temperatures of the calibration buffer and samples should not deviate by more than 1°C (SFS 13037 2011, 6.). The HI98168 handheld meter was calibrated at 21.5°C , while the FEP20 benchtop meter was calibrated at 22.5°C . Examining the average temperature of the samples listed in Table 13, sample D, dried, had an average temperature of 23.6°C , which deviates by more than 1°C from the calibration temperature of meter FEP20.

Another cause of variation in the measurements regarding pH could have been caused by the use of deionised water. Deionised water can raise the electrical resistance in the medium in which the pH is measured. This can occur if the conductivity of the deionised water is under $50\ \mu\text{S}/\text{cm}$. (Bösche & Schleicher n.d., 5) The water used for measurements was grade 2, which has a conductivity of $<1\ \mu\text{S}/\text{cm}$.

Another factor to consider is the biological stability of the sample media. Biodegrading organic materials under aerobic conditions yields compost. The greater the maturity of the compost, the slower its microbiological activity since the microorganisms have used all readily available material. As the samples A, B, and C's activity varies due to their different maturity, so does the microbiological activity. Since the samples were not analysed in a single day due to insufficient manpower, the pH of the samples may have changed due to microbial activity.

Alternately, the variation might be the result of the used approach. The technique used with the HI981030 pen tester and the HI98168 handheld meter was direct soil measurement, which needed no sample preparation beyond pre-poking the sample with a small soil auger and, if necessary, moistening the sample with a small quantity of deionised water. The technique employed with the FEP20 benchtop meter conformed to EN 13037:2011, which needed specific sample preparation. In addition, the probes of the devices vary in characteristics like measurement precision, internal reference electrolyte, junction type, and glass membrane shape.

Regarding time utilisation to carry out calibration and measurements that include four (4) samples and four (4) replicas of each sample, it can be seen in Table 13 that the method of direct measurement is more resource-efficient with a time utilisation of about 65 min to 70 min in comparison to the method in accordance with EN 13040:2011, which requires a time utilisation of about 4 h and 55 min when using un-dried samples and about 5 h and 55 min when using dried samples. However, since the time utilisation was only recorded once, it should be interpreted as a directional reading.

5.2 Analysis of Device Characteristics

Operationally, the instruments are all not complicated to use. However, in laboratory use, the HI98168 handheld meter and the FEP20 benchtop meter offer

better accuracy and more calibration points than the HI981030 pen tester. In addition, the HI981030 pen tester does not display temperature and calibration efficiency. For accurate laboratory analysis, a pH meter needs to display calibration efficiency since it translates the condition of the probe; also, a pH value without a temperature value is incoherent. Therefore, this type of pH meter is suitable for conventional use.

From a sustainability viewpoint, the HI981030 pen tester is a disposable device since it cannot be replaced in the case of probe damage. On the other hand, the HI98168 handheld and the FEP20 benchtop meter probes can be replaced and are compatible with other probes. In addition, both devices can store the measured data and transfer it to a computer. The HI98168 handheld meter may also be used in the field.

6 CONCLUSION

This research aimed to evaluate whether a field pH meter can be used to monitor soil and compost pH as a more resource-efficient alternative to the laboratory approach outlined in EN 13040:2011.

In light of the findings obtained with regard to pH, it would seem that none of the methods or measurement devices could be considered better than the others. However, due to a lack of temperature and calibration information, the HI981030 pen tester was determined to be unsuitable for laboratory usage.

On the other hand, the HI98168 handheld meter was considered adequate since it includes advantageous characteristics such as ATC, up to five-point calibration, an operating range of -5 to 70°C, an accuracy of 0.01 pH, and the ability to record up to 100 readings on demand, and the meter alerts about probe difficulties. Additionally, the probe (HI12923) is designed for measuring dry soil. Furthermore, it may be used with different types of probes, making it versatile. Considering the time necessary to conduct a series of pH measurements as in this research, it can be stated that the method of direct soil pH measurements seems to be more resource-efficient than the method specified in EN 13040:2011.

To conclude, it seems like there is a potential for a field pH meter to be used in a laboratory environment to monitor soil and compost. However, it would be interesting to conduct future research to establish the reason for the variance in the pH values. Multiple independent variables, comprising calibration, measurement temperature, measuring medium, methodology, probe features, and human resources constraints, were identified as potential sources of the discrepancy.

To rule out the variables previously mentioned, the following should be considered when conducting future research on this topic: when testing over a

wide range, like in this study, it is best to calibrate the device at three points to get the most accurate results. The sample and the calibration temperature must differ by no more than 1°C. Compost is an active measurement medium since biodegradation is constantly happening, which may alter the pH value. Therefore, when comparing the pH defined by two methods, such as direct soil measurement and pH determination in a suspension, it is advisable to perform the measurement simultaneously to rule out the effects of biodegradation. In addition, it is advisable to extend the test setup by analysing the sample prepared according to the principle of the European Standard EN 13040:2011 with a direct soil pH meter to determine if the method or probe characteristic affects the variables.

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APPENDICES

Appendix 1. Un-dried sample mass

Date: 10.6.2021	Un-dried sample volume 30 mL in g					Un-dried Sample mass [g] for pH measurements			
Sample	1 replica	2 replica	3 replica	4 replica	Average sample mass [g]	1 replica	2 replica	3 replica	4 replica
A	8.45	8.79	7.41	7.27	7.98	8.00	7.98	8.00	8.00
B	8.31	8.72	8.33	8.22	8.40	8.40	8.44	8.44	8.41
C	9.53	9.56	8.81	9.53	9.36	9.39	9.34	9.36	9.36
D	14.79	14.40	14.00	13.45	14.16	14.16	14.16	14.17	14.18

Appendix 2. Dried sample mass

Date: 15.6.2021	Dried Sample volume 25 mL in g					Sample mass [g] for pH measurements			
Sample	1 replica	2 replica	3 replica	4 replica	Average Sample mass [g]	1 replica	2 replica	3 replica	4 replica
A	8.59	8.75	9.37	9.04	8.94	8.99	8.93	8.99	8.94
B	8.11	8.22	7.67	7.78	7.95	7.95	7.95	7.93	7.98
C	7.93	8.89	7.63	8.02	8.11	8.19	8.12	8.11	8.13
D	17.83	20.51	17.82	18.49	18.66	18.63	18.61	18.65	18.64

Appendix 3. Un-dried sample pH measurements

Date 10.06.21	pH Measurements with Un-dried Sample						Temperature [°C]					
Sample	1 replica	2 replica	3 replica	4 replica	Average pH	σ	1 replica	2 replica	3 replica	4 replica	Average temperature [°C]	σ
A	6.87	6.87	6.81	6.75	6.83	0.057	23.8	23.5	23.3	23.0	23.4	0.337
B	8.12	8.04	8.05	8.07	8.07	0.036	22.6	22.8	22.8	23.0	22.8	0.163
C	8.71	8.78	8.76	8.74	8.75	0.030	23.0	22.7	23.3	23.2	23.0	0.265
D	4.36	4.44	4.46	4.46	4.43	0.048	22.7	23.0	22.9	22.8	22.9	0.129

Appendix 4. Dried sample pH measurements

Date: 15.06.21	pH Measurements with Dried Sample						Temperature [°C]					
Sample	1 replica	2 replica	3 replica	4 replica	Average pH	σ	1 replica	2 replica	3 replica	4 replica	Average temperature [°C]	σ
A	6.55	6.52	6.54	6.55	6.54	0.014	23.4	23.0	23.1	23.1	23.2	0.173
B	7.83	7.83	7.83	7.84	7.83	0.005	23.1	23.0	22.8	22.8	22.9	0.150
C	8.20	8.24	8.19	8.21	8.21	0.022	23.0	23.3	23.9	23.9	23.4	0.458
D	4.37	4.40	4.39	4.40	4.39	0.014	23.8	23.7	23.4	23.3	23.6	0.238

Appendix 5. Direct soil pH measurements

Date: 14.6.2021		Instrument																	
		HI981030						HI98168											
Sample		pH						pH						Temperature [°C] measured with HI98168					
		1 replic a	2 replic a	3 replic a	4 replic a	Average pH	σ	1 replic a	2 replic a	3 replic a	4 replic a	Average pH	σ	1 replic a	2 replic a	3 replic a	4 replic a	Average temperature [°C]	σ
A		5.96	5.98	5.92	5.88	5.94	0.0 44	5.79	5.92	5.87	5.71	5.82	0.0 92	21.6	22.0	22.1	22.0	21.9	0.2 22
B		7.49	7.38	7.34	7.36	7.39	0.0 67	7.11	7.32	7.12	7.29	7.21	0.1 10	21.9	22.2	22.0	22.3	22.1	0.1 83
C		8.81	8.83	8.86	8.92	8.86	0.0 48	8.70	8.68	8.64	8.72	8.69	0.0 34	22.3	22.4	22.3	22.3	22.3	0.0 50
D		4.04	4.13	4.00	4.18	4.09	0.0 82	4.23	4.21	4.25	4.47	4.32	0.1 33	21.9	21.8	21.5	21.7	21.7	0.1 71

Appendix 6. Calibration time

	Instrument		
	FEP20	HI98168	HI981030
Calibration	Calibration time [hh:min:ss]		
Calibration 1	00:15:32	00:14:08	00:20:17
Calibration 2	00:16:42	00:13:15	00:15:00
Calibration 3	00:18:10	00:20:04	00:17:40
Calibration 4	00:15:05	00:15:00	00:14:20
Average calibration time	00:16:22	00:15:37	00:16:49
σ	00:01:23	00:03:03	00:02:43