Microchemical Journal 111 (2013) 47–52

Contents lists available at SciVerse ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Evaluation of some wet digestions methods for reliable determination of total phosphorus in Australian soils

Benjamin Webb, Samuel B. Adeloju *

NanoScience and Sensor Technology Research Group, School of Applied Sciences and Engineering, Monash University, Gippsland Campus, Churchill, Victoria 3842, Australia

ARTICLE INFO

Article history:
Received 30 June 2012
Received in revised form 27 January 2013
Accepted 1 February 2013
Available online 9 February 2013

Keywords:
Phosphorus
Total P concentration
Soil
Wet digestion
Acid digestion

ABSTRACT

Four common wet digestion methods have been evaluated for reliable determination of total phosphorus (P) concentrations in soil samples. Wet digestion of soil samples with nitric acid gave the highest recovery of total P concentrations with a percentage recovery of 90.1 ± 0.9% (n = 3). A lower percentage recovery of 87.0 ± 1.4% (n = 3) was achieved by wet digestion of soil samples with sulphuric acid. The use of acid mixture or acid–alkaline mixture for wet digestion of soil samples gave phosphorus recoveries of 82.4 ± 1.9% (n = 3) and 85.4 ± 2.1% (n = 3) with nitric acid–sulphuric acid mixture and nitric acid–potassium persulphate mixture, respectively. Substantial improvement in phosphorus recoveries with wet digestion of soil samples with sulphuric acid was achieved by further treatment of digested soil samples with sulphuric acid, resulting in a recovery of 92.8 ± 1.0% (n = 3), which was higher than possible with other acid and mixtures. The wet digestion of soil samples with sulphuric acid was also the only method which met reactivity and safety considerations. The successful utilisation of wet digestion with sulphuric acid for reliable determination of total P concentrations in a range of soil samples from some Australian dairy and beef rearing pastoral land is reported.

1. Introduction

Phosphorus (P) is an essential nutrient in natural ecosystems and it is also critically important to agricultural systems [1–6]. It is required for many agricultural processes including photosynthesis, nitrogen fixation, flowering, seeding and fruit maturation [3–6]. Soils in most parts of the world are low in P and deficient for optimal agricultural production [1,4–8]. This deficiency is often compensated for by applying various sources of P to soil, and thereby increasing the P status of the soil and its agricultural yield.

Unfortunately, this mode of addition of P to soils has also had severe and detrimental effects on several waterways around the world, leading to an increased rate of eutrophication [9–12] and common presence of algal blooms which have been associated with various problems in fish, livestock and human health [4,12–14]. The presence of phosphorus (as phosphate) and nitrogen (as nitrate) has also been implicated in many cases with several reported outbreaks of blue-green algae which can have devastating effects on waterways.

A very good indication of the soil P pools and management practices that may contribute to P enrichment of runoff and waterways can be obtained by conducting soil P measurements [5,6,12,15–17]. These measurements provide a basis for matching P inputs and agricultural crop demands [1,5,6,18]. Soil P measurements have been used to assess both environmental and agronomic impacts of P concentration extractable from soil [6,18–21].

Total P concentration in soil is an important parameter which accounts for all forms of P within the soil. This parameter is often used to determine soil P status for phosphorus based fertiliser application and for estimation of P exports or agricultural yield [5,6,22]. It also provides a useful indication of the overall and potential nutrient supply of P, and has been used in relationship comparisons with other soil measurements. However, total P measurement is limited in that it does not differentiate between plant available P and non-available sources, such as organically bound from insoluble mineral P [23]. Nevertheless, it is still a very significant parameter for both environmental and agronomic considerations. The reliable determination of total P concentrations in soil is however not easy. It requires adequate and effective decomposition of the soil matrix to ensure complete release of P into solution prior to analytical measurement.

A number of digestion methods have been proposed for the determination of total P concentrations in soil. In one method, Tan [24] used a fluoro-boric acid digestion which employed a specialised bomb digestion vessels and hydrofluoric acid. The original version of this method [25] also required specialised platinum crucibles and utensils for sodium hydroxide or sodium carbonate fusion [24]. Olsen and Sommers [26] also proposed a sodium carbonate fusion method, and this again required specialised platinum equipment. Another suggestion from Olsen and Sommers [26] involved wet digestion of soil with a perchloric acid. This method was not only complex, but had a range of safety issues and required a specialised perchloric acid fumehood. For these reasons, this digestion method is rarely used, except in specialised laboratories with adequate perchloric acid fumehood. Due to safety concern, some of the available soil method handbooks have

* Corresponding author. Tel.: +61 3 9902 6450; fax: +61 3 9902 6738.
E-mail address: Sam.Adeloju@monash.edu (S.B. Adeloju).

0026-265X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.microc.2013.02.001

deliberately not included methods that employ perchloric acid [23]. However, it is important to note that safety consideration is not only limited to the use of perchloric acid, but also to the reactivity of some acids and/or mixtures to soil samples.

In another study, Dick and Tabatabai [27] reported on the use of a sodium hypobromite/sodium hydroxide solution for total P determination in soil samples. The mixture was heated to dryness on a sand bath at 260 °C, followed by addition of formic acid and sulphuric acid. Bowman [28] also used ordered additions of sulphuric acid, hydrogen peroxide and hydrofluoric acid to decompose soil samples for total P determination. Both of these methods require considerable manipulation of the sample and are labour intensive compared to other methods [29].

The examples cited above highlight the current state of play with the determination of total P concentrations in soil. This is obviously not ideal for such a significant parameter which is highly important in assessing the inputs of P into farmland and waterways. In general, most of the currently available methods require specialised laboratory conditions or equipment, dangerous chemicals and intensive labour. To address this issue and ensure ease of attainment of reliable total P concentrations, there is a need for the development of a simpler soil digestion method that can be readily employed within standard laboratory conditions without safety concern, complex and laborious processes.

This paper reports on a thorough evaluation and assessment of four wet digestion methods carried out to enable identification and/or development of a simple and direct approach for pre-treatment of soil samples for reliable determination of total P concentrations. The wet digestion methods considered are those that are readily used for determination of other substances and that require the use of simple laboratory equipment, glassware and reagents [30,31]. The adequacy, efficiency and choice of the digestion methods were assessed on the basis of recovery efficiencies for total P concentration in soil samples, the ease of use, reproducibility and safety consideration. The application of the chosen method to the reliable determination of total P concentration in a wide range of soil samples from two intensive agricultural areas was also considered.

2. Materials and methods

2.1. Reagents and standard solutions

All acids and reagents used were of analytical reagent grade solutions. All solutions were prepared and diluted with distilled deionised water (18 MΩ cm, Millipore, MA, USA).

Nitric acid (0.01 M) used for adjusting the pH was prepared by diluting concentrated nitric acid with distilled deionised water. Stock phosphate solution (1000 mg P/L) was prepared by dissolving 4.393 g of potassium di-hydrogen orthophosphate in 1 L of distilled deionised water. A standard phosphate solution (100 mg P/L) was prepared by diluting an aliquot of this solution further with distilled deionised water.

2.2. Instrumentation

All phosphate analyses were carried out by using an adapted method (SmartChem 140 Method 420-3651) modified for use with soil samples on the Westco SmartChem 140 automated wet chemistry discrete analyser (Westco Scientific Instruments, Inc., Brookfield, CT, USA). This method utilises an antimony–phospho-molybdate complex formed through the reaction of ammonium molybdate, antimony potassium tartate and dilute phosphorus solutions in an acid medium. Ascorbic acid is added to reduce the complex to produce a blue coloured complex measured at 880 nm. The resulting absorbance increased proportionally to P concentration in solution. The normal sample and reaction diluant in the method was deionised water, but was changed in this study to 0.01 M nitric acid to match the acidity of diluted sample digest.

2.3. Glassware

All glassware and other containers were washed, soaked in a 2 M nitric acid for at least 7 days, rinsed three times with deionised water, soaked in deionised water and finally soaked in 0.1 M hydrochloric acid (HCl) until ready for use.

2.4. Heating sources

Standard laboratory hotplates with aluminium surfaces were used for heating samples. The maximum temperature setting was used for each of the methods or as safety permitted. The temperatures of the extracts were recorded and their significance for sample digestion is discussed later.

2.5. Sample collection and preparation

Soil samples were collected from an irrigation bay (width 30 m, length 300 m) at the Macalister Research Farm (38°00′S 146°54′E), a dairy farm situated in the Macalister Irrigation District of south-east Victoria (Australia). The soil was a natric grey Sodosol [32] and carried pastures that contained perennial ryegrass (*Lolium perenne*), white clover (*Trifolium repens*) and assorted invasive species including dock (*Rumex* spp.) and distichum (*Paspalum paspaloides*) [11,33].

200 samples of 20 mm cores and 30 samples of 100 mm cores were collected from the sampling sites using a grid pattern. The soil cores were bulked for each depth to provide a composite sample for the sampling location. After collection, the soil was stored (4 °C) in polyurethane bag and transported to the laboratory. The bulked soil cores were air dried (40 °C), ground and passed through a 2 mm sieve. Samples were then stored in polyethylene containers at ca. 20 °C prior to analysis.

Other soil samples were collected from selected agricultural sites within south-east Victoria, from 2 areas known as Maffra and Warragul. These areas were selected as geographically close agricultural areas (approximately 120 km range) with varying agricultural management practices, particularly irrigation application. A total of 14 sites were sampled, seven from each of the two areas. Soils were classified using an Australian soil classification system. The 7 sites in Warragul were of three different soil classifications, as indicated later in the results. The 7 sites in Maffra were also of 3 different soil classifications, as indicated later in the results.

2.6. Soil moisture content

The moisture content was determined by heating the soil samples in a drying oven at 105 °C, cooled in desiccators and weighed repeatedly until a constant mass was obtained. The total P concentrations for each sample replicate were corrected for soil moisture content.

2.7. Digestion methods

Four wet digestion methods were investigated for reliable determination of total P concentrations in soil samples. These methods were adapted from those reported previously by Adeloju et al. [30,31] for trace metal analyses. Digestion of each sample was carried out in triplicate. The specific soil digestion procedures for each of the wet digestion methods are described as follows:

Method A: *Nitric acid* (HNO_3) *digestion*: 0.3 g of soil sample was accurately weighed into a 100 mL Erlenmeyer flask. The flask containing sample was then transferred to a fumehood, where 10 mL of HNO_3 (70%) was added and a glass funnel was inserted into the neck of the flask. The mixture was heated on a hotplate to approximately 125 °C where nitrogen oxide fumes were evolved and the volume of the mixture was reduced to approximately 2 mL. The flask was then