



Spectrophotometric methods for the measurement of soil pH: A reappraisal

Emanuele Fornasier^a, Flavio Fornasier^b, Valerio Di Marco^{a,*}

^a Department of Chemical Sciences, via Marzolo 1, 35131 Padova, Italy

^b CREA-VE, Via Trieste 23, 34170 Gorizia, Italy

ARTICLE INFO

Article history:

Received 23 March 2018

Received in revised form 31 May 2018

Accepted 7 June 2018

Available online xxxx

Keywords:

pH

Soil

UV-visible

Spectrophotometry

Glass electrode

ABSTRACT

The pH of aqueous soil extracts is generally measured potentiometrically by glass electrode (GE). Spectrophotometric methods have also been used till around the '80s, and then they have apparently been abandoned. However, the use of microplates and spectrophotometers able to read absorbance values in them can significantly increase the speed of the data collection (saving analysis time), thus justifying their reappraisal. Three spectrophotometric methods are proposed in this work: a one-indicator (OISM), a separated three-indicator (STISM) and a mixed three-indicator (MTISM) spectrophotometric method. They are based on the addition of one or three colorimetric indicators (methyl red, bromocresol violet, and bromothymol blue) to the aqueous extract. The pH is measured through its absorption properties in the visible region. The analysis of 60 soil samples showed that STISM and MTISM results correlate well with the ones obtained by GE. The STISM method, being more simple and general than the other two methods, is proposed for quick routine analyses. The repeatability, reproducibility and accuracy of STISM (and of GE, for comparison) were evaluated by measuring several times the pH of a series of soil samples and of a certified reference soil. The standard deviations of STISM results were slightly worse than those of GE, whereas the accuracy was slightly better, indicating that STISM and GE have overall similar performances. STISM method is much faster than GE one: the analysis time saving is around 2 min per sample, and it becomes very high when hundreds of samples have to be analysed. It follows that STISM can represent an advantageous alternative to GE for rapid and accurate soil pH measurements.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Soil pH is considered to be the most informative soil parameter [1–3]. It has great influence on the growth of several plants [4–6], and also the sorption and the transport of pollutants in soils, e.g. pharmaceuticals [7], has been demonstrated to depend on pH. Soil pH is becoming a main concern as regards to global soil acidification, because it appears to be correlated to the observed fertility reduction over time [8].

Despite soil pH mapping can be extremely useful when performed over a continental distance scale [9], the local pH values often differ significantly within very short distances (meter down to millimeter resolution) [10]. A detailed space resolved pH measurement should be performed for each field, which requires a very large number of measurements. The number of samples to be analysed can easily exceed several hundreds [11]. Measurements can be reduced with the help of interpolation methods [12], but the development of rapid, cheap and accurate methods for the experimental measurement of soil pH is continuously pursued [13].

The measurements of pH of soils are mainly based on the use of a glass electrode (GE), and are performed in the aqueous solution obtained after extraction of the soil [14–18]. The pH measurements performed by GE with the recommended procedures [14] are considered accurate and relatively cheap. However, for each sample a significant measuring time is required, because the GE response is generally not very rapid, and the electrode must be cleaned and/or rinsed each time when the solution is changed. Automatic methods have been proposed involving GE and in some cases also the recommended procedures, in which the analysis time is reduced ([19] and references therein). Another reason of concern for potentiometric measurements by GE regards the effective accuracy of the obtained pH values, which may be affected by significant errors. For example, the GE stabilization times indicated by common procedures might be largely insufficient, as demonstrated by Than et al. [20]. Also other passages in the procedure, e.g. shaking and drying, may affect significantly the measured pH [21]. The occurrence of uncertainties in GE measurements were confirmed by a multilaboratorial study performed by Kalra [14], which included 53 laboratories analyzing the pH of the same twenty samples. Although the same pH-potentiometric procedures were used, pH differences detected by different laboratories on the same sample very often

* Corresponding author.

E-mail address: valerio.dimarco@unipd.it (V. Di Marco).

exceeded 0.3 log units, and not rarely they were around one pH unit, strongly suggesting that different GE give different soil pH values.

A number of papers have appeared in the literature (even very recently), where methods are proposed to obtain soil pH data without using GE. For example, electrodes based on PVC-based pH sensors with flow injection analysis [22], ISFET [23], quinhydrone [24], modified glass [25] and antimony oxide [13] have been used. Spectroscopy represents another promising alternative for the measurement of soil pH. The used spectroscopic methods are diffuse reflectance in the visible-infrared [26], also in conjunction with digital photography [27], X-ray fluorescence [28], fluorescence of pH sensitive indicator dyes [10] and laser-induced breakdown spectroscopy [29]. Around or before the 1980's, many authors proposed and used spectrophotometric methods based on the addition of a colorimetric indicator to the aqueous extract, and measured the soil pH through the indicator absorption properties in the visible region. To the best of our knowledge, the latest papers of this kind have been published by Qiu et al. [30, 31]. All methods showed good results but then they have apparently been abandoned. The possible reason for this is that these spectrophotometric methods did not present advantages over the GE ones, and in particular the former were as time-consuming as the latter. Nowadays, however, a significant time saving can be expected for spectrophotometric methods compared to GE, thanks to the availability of microplates and spectrophotometers able to read absorbance values in them. This allows performing many pH measurements of microliters amounts of aqueous soil extracts in a few time. Alternatively, measurements can be rapidly performed by optical fiber spectrophotometers.

In this paper, three new spectrophotometric methods are proposed for the measurement of soil pH, based on the addition of colorimetric indicators. Differently than it was made in the previously proposed procedures, not only microplates are used, but also the co-addition of more than one indicator is considered for measuring soil pH values, in order to cover the whole possible soil pH range. The most effective spectrophotometric method was then validated by performing repeatability and reproducibility measurements, and by analyzing a certified reference soil.

2. Experimental

Reagents used were milliQ water (Millipore), calcium chloride (Carlo Erba, 99%+), hydrochloric acid (Carlo Erba), sodium hydroxide (Sigma-Aldrich), methyl red (MR, Carlo Erba, ACS), bromocresol violet (BV, Sigma Aldrich), bromothymol blue (BB, Sigma Aldrich, ACS), dimethyl sulfoxide (DMSO, 99.5%, GC grade Riedel-de Haen-Sigma cat 60,157). Buffers at pH = 3.00, 4.00, 6.00, 7.00, 8.00, 9.00 were purchased from Honeywell Fluka (cat 31,046, 33,643, 33,545, 33,646, 33,547, 33,648, 33,649, respectively); buffer at pH 5.00 was purchased from Labochimica, Italy (cat 7852). The instruments were a pH-meter (VTW inoLab Level 3) equipped with a combined glass electrode (GE) (Mettler-Toledo InLab Semimicro), a BIOTEK Synergy HT spectrophotometer equipped with a microplate Hellma (quartz, 96 wells), a horizontal stirrer (IKA HS 501), and two centrifuges (Heraeus Megafuge 1.0R and Hettich MIKRO 200R). UV-visible spectra for solutions containing each indicator alone were measured at acidic (HCl 0.01 M) and basic (NaOH 0.01 M) pH and at an indicator concentration of 10^{-5} M with a Perkin Elmer Lambda 25 Precisely.

For the soil pH measurements, 600 mg of air-soil are put in a 2 mL Eppendorf tube together with 1.5 mL extracting aqueous solution freshly prepared, and stirred at 200 Hz for 2 h. The Eppendorf tubes are then centrifuged at 20000g for 4 min. From each tube, four aliquots (200 μ L each) of the supernatant solutions are transferred to the microplates. Absorbance of soil extract with no indicator was recorded and it was used as blank. Subsequently, the following additions are performed: 2 μ L of a $1.5 \cdot 10^{-3}$ M methyl red (MR) solution in DMSO to the first aliquot, 2 μ L of a $1.5 \cdot 10^{-3}$ M bromocresol violet (BV) solution in DMSO to the second aliquot, 2 μ L of a $1.5 \cdot 10^{-3}$ M bromothymol blue

(BB) solution in DMSO to the third aliquot, and 2 μ L of a DMSO solution containing $1.0 \cdot 10^{-3}$ M MR, $1.5 \cdot 10^{-3}$ M BV and $1.5 \cdot 10^{-3}$ M BB to the fourth aliquot. These four aliquots contain therefore 15 μ M MR, 15 μ M BV, 15 μ M BB, and 10 μ M MR + 15 μ M BV + 15 μ M BB, respectively. The GE was previously calibrated by the buffers at pH = 4.00 and 7.00. The electrode response is verified every 10 samples by measuring the pH in the calibration buffer. All aliquots are transferred to the microplates, and absorbance values at selected wavelengths are measured, or the whole UV-visible spectra (3 nm resolution, range 300–700 nm) are recorded. For some samples pH was measured also by GE before the indicator additions. Spectrophotometric data have been treated by the softwares Microsoft Excel 2016 and Worfram Mathematica.

The effect of the indicators on the soil pH was evaluated on four soils (labelled A, B, C, D) of different characteristics and pH as described in Table S1 (Supporting information). The pH correlations between the indicator methods and the GE were evaluated on 60 unknown soil samples taken in a field where a soil pH gradient (3 pH units) occurred at a distance of just 20 m. The field was located in Premariacco, Friuli region, Northeastern Italy. Method repeatability was evaluated by analyzing 18 different soil samples in the same day, in the same laboratory, with the same procedure and by the same operator, and by repeating the measurements 10 times for each sample in the shortest time as possible. The 18 soil samples (Australia 1, Australia 2, Piemonte 1, Piemonte 2, Bari, Monte Faito, Moruzzo, Doberdò, Foggia, Lodi, Reana, Reana grass, Bueriis, Sobretta A, Sobretta B, Sobretta C, Cesarolo, CRM 497) originated from Italy except the first two (Australia 1 and Australia 2) and the last (certified reference soil); all samples are arable soils except Monte Faito (forest), Reana grass, and Sobretta A, B, C (forest). Reproducibility was tested by performing the same procedure on six samples after two months. The certified reference soil CRM 497 (Sigma-Aldrich, certified pH = 6.15, confidence interval ± 0.07 , prediction interval ± 0.42 , Anab accredited) was included to evaluate method accuracy.

3. Methods

Three spectrophotometric methods are proposed: a one-indicator (OISM), a separated three-indicator (STISM) and a mixed three-indicator (MTISM) spectrophotometric method.

3.1. One-Indicator Spectrophotometric Method (OISM)

If a monoprotic colorimetric indicator is added to a solution containing no other absorbing species, the measured absorbance at the wavelength λ is given by:

$$A_{\lambda} = \varepsilon_{\lambda, \text{HIn}} b [\text{HIn}] + \varepsilon_{\lambda, \text{In}} b [\text{In}] \quad (1)$$

where [HIn] and [In] are the concentrations of the protonated (HIn) and deprotonated (In) indicator (charges are omitted for simplicity), $\varepsilon_{\lambda, \text{HIn}}$ and $\varepsilon_{\lambda, \text{In}}$ are their absorptivity coefficients at the wavelength λ , and b is the optical length. If the indicator is polyprotic, Eq. (1) is changed by replacing [HIn] with $[\text{H}_n\text{In}]$, [In] with $[\text{H}_{n-1}\text{In}]$, and considering the proper ε values; the subsequent equations remain the same as for the monoprotic indicator, if at any pH the concentration of all protonation states but two can be neglected.

From the mass balances of the indicator, [HIn] and [In] can be expressed as a function of C (total concentration of indicator), $a_{\text{H}_3\text{O}^+}$ ($=10^{-\text{pH}}$), and K_a (acidic constant of the indicator):

$$[\text{HIn}] = C \frac{a_{\text{H}_3\text{O}^+}}{K_a + a_{\text{H}_3\text{O}^+}} \quad [\text{In}] = C \frac{K_a}{K_a + a_{\text{H}_3\text{O}^+}} \quad (2)$$

Download English Version:

<https://daneshyari.com/en/article/7667618>

Download Persian Version:

<https://daneshyari.com/article/7667618>

[Daneshyari.com](https://daneshyari.com)