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Hybrid flow system integrating a miniaturized optoelectronic detector for on-line dynamic fractionation and fluorometric determination of bioaccessible orthophosphate in soils



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ABSTRACT

An integrated Sequential Injection (SI)/Flow Injection (FI) system furnished with a miniaturized LED-based fluorometric detector is presented in this work for expedient bioaccessibility tests of orthophosphate in soils. Equipped with a microcolumn of conical shape containing 50 mg of soil, the hybrid flow system was resorted to on-line dynamic leaching and real-time quantification of pools of mobilizable orthophosphate using a bi-directional syringe pump and multiposition valve. The flexibility of the flow manifold was harnessed to explore both bi-directional and uni-directional flow extraction modes with the added degree of freedom of on-line dilution of extracts whenever needed. Bioaccessible orthophosphate was split in three fractions, the so-called NH_4Cl fraction containing labile exchangeable phosphates, the alkaline fraction with Fe and Al-bound phosphates and the acidic fraction containing Ca-bound phosphates.

The prevailing molybdenum blue photometric detection method is replaced by spectrofluorometric detection based on the ion pair formation between the phosphomolybdate heteropolyacid and rhodamine B with the subsequent quenching of the dye fluorescence. The dedicated optoelectronic detector was integrated in a secondary FI manifold and operated according to the fluorometric paired emitter–detector diode (FPEDD) principle involving two light emitting diodes as fluorescence inductors and one as detector of LED-induced fluorescence.

Demonstrated with the analysis of a standard reference material (SRM 2711) and a real agricultural soil, the developed FI/SI fractionation system with FPEDD detection is proven reliable against the standard molybdenum blue method ($p > 0.05$), and useful for investigation of the leaching kinetics of orthophosphate in bioaccessibility tests through in-line recording of the extraction profiles.

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1. Introduction

Phosphorus plays an important role in the environment and food web as is contained in fertilizers for supporting the plant growth and in food additives as well. On the other hand, phosphorus is a factor of eutrophication in water reservoirs, such as lakes or rivers, and might pose severe risks to aerobic living organisms [1]. Phosphorus occurs in different forms – both inorganic, namely orthophosphates, metaphosphates and polyphosphates, and organic species [2–4], which include e.g. phospholipids, sugar phosphates, nucleic acids and phosphoproteins [5]. The labile organic forms of phosphorus might hydrolyze on a

short notice [6]. Immediate detection is thus needed after sampling or leaching for discrimination between inorganic and organic phosphorus species. This requirement is most likely met with flow analysis methodology [7]. In case of soil analysis in-line microcolumn/chamber extraction coupled to downstream detection allows the simplification of the analytical leaching procedures for orthophosphate and the minimization of the hydrolysis of the organic forms [8,9].

Free inorganic phosphorus forms can be measured using different analytical methods including potentiometry [10], voltammetry [11] and amperometry [12] but the most commonly used are optical methods in combination with the molybdenum blue chemistry. Flow methods have been frequently used in view of their green chemical credentials as a result of miniaturization, automation, high sample throughput with the extra degree of on-line sample handling at hand [13,14]. A large number of FI and SI methods focused on detection of

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the yellow heteropolyacid complex (phosphomolybdate acid) generated by reaction of orthophosphate with molybdate in acidic medium [13–15], yet this method is deemed not sensitive enough in multifarious environmental analysis. Sensitivity amelioration is gained by reducing the heteropolyacid to the molybdenum blue dye using ascorbic acid, tin (II) chloride, hydrazine or hydroquinone [14–16]. The molybdenum blue method was also used in combination with enzymatic reactions based on alkaline phosphatase to determine orthophosphate [17] and flow-based preconcentration setups using anion-exchange reactors [18]. Another existing photometric method for determination of orthophosphate is based on the ion-pair association between the yellow heteropolyacid and Malachite Green, yet it affords poorer repeatability and narrower linear range as compared to the molybdenum blue chemistry [13]. Besides photometric methods fluorometric detection is also feasible on the basis of the ion-pair formation between the heteropolyacid and fluorophores, such as rhodamine B [13,19] and rhodamine 6G [20,21] for indirect analysis relying upon fluorescence quenching. This procedure has been adapted to a flow-based format as well [13,14,19–21].

In this work, the concept of light-emitting diodes (LEDs) as both emitters and detectors of light (so-called paired emitter-detector diode (PEDD) device) is used. This idea has been recently launched but deemed prospective. New LED-based miniature detectors have thus been constructed and dedicated to particular analytical applications with no need of optical filters. LEDs are extremely affordable what makes the cost of PEDDs really low. They are also stable, sturdy, highly efficient and feature long-term operation. Furthermore, LEDs need not that much power to elicit light. Two additional merits are the narrow-band light emission (width at half maximum averages 20 nm) and their versatility with commercially available LEDs from UV to NIR spectral range.

The LED working as detector should operate in reversed mode. The current produced on this LED however is too small to be measured. Diamond's team was the first in building an optical detector based on paired LEDs, measuring the time of discharge of the LED detector [22,23]. Further research was done to improve the way of measurements of the analytical signal generated by PEDDs [24,25]. The voltage has also been used as analytical readout, which is proportional to the light intensity, and correlates with the concentration of analyte as described by the Shockley's diode equation and the Lambert-Beer-Bouguer law [24]. Critical comparison of LEDs against photodiodes as detectors has been recently reported by Hauser's team [26].

PEDDs are predominantly developed for photometric measurements and several research teams utilized this concept to build miniaturized detection platforms for analytical purposes [27–31]. LEDs can also be used as fluorescence inductors in dedicated cell geometries. Only recently, prototypes of fluorometric PEDD (FPEDD) have been reported [32–37]. FPEDD detectors are greatly cost-effective and miniaturized in comparison to conventional fluorometric spectrometers. These detectors are dedicated to a given analysis by careful selection of the optical properties of the LEDs. Enhancement of sensitivity of measurements is provided by using various diodes (with the same emitting wavelength) as fluorescence inductors and one LED working as detector of induced fluorescence [33]. Such optoelectronic detectors have been successfully used in fluorometric assays of calcium [33], phosphate [34], oxygen [35], riboflavin [36] and proteins [37].

A novel hybrid SI/FI system integrating in-line soil leaching (using the Hieltjes-Lijklema sequential extraction procedure) with flow-through FPEDD detection (using two LED emitters) is herein proposed for expedient bioaccessibility tests of orthophosphate in soils. To the best of our knowledge PEDD detection has not been resorted to the analysis of soil extracts as of yet. As compared to previous dynamic leaching methods for orthophosphate using advanced flow methodology [9,38] the proposed setup is more

simple (merely needs one syringe pump instead of five liquid drivers [9]) and uses portable and affordable detection systems that are easily constructed in the lab. Combining an SI manifold for automatic leaching and a secondary FI system for on-line detection the phosphorus laden extracts are analyzed at real-time, with the subsequent minimization of the hydrolysis of organic phosphorus in the alkaline or acid fractions that was not avoided in previous studies with off-line detection of leachates [38]. The hybrid flow system also affords in-line dilution upon demand by using automatic flow programming.

2. Experimental

2.1. Reagents, solutions, samples

All chemicals were of analytical reagent grade. Solutions were prepared using double distilled water. The stock standard solution (100 mg PO_4^{3-} /L in water) was prepared from KH_2PO_4 (Merck). Working standard solutions were prepared separately in each extractant milieu (NH_4Cl , NaOH , HCl). In this work, the three-step Hieltjes-Lijklema (HL) sequential extraction procedure [39] was selected. In the first step, 1.0 mol/L NH_4Cl (Probus) adjusted to $\text{pH}=7$ with $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25%, Scharlau) was used to extract the labile phosphate (water soluble and exchangeable fraction) from the soil sample. In the second step, 0.1 mol/L NaOH (Panreac) was pumped through the column to extract the Fe- and Al-bound phosphate. The last step, using 0.5 mol/L HCl (37%, Scharlau) as extractant, released Ca-bound phosphate. The derivatization reagent consisted of 12 g/L ammonium molybdate tetrahydrate (Scharlau) in 0.8 mol/L H_2SO_4 (Sigma-Aldrich). In some instances oxalic acid (Panreac) was added at the level of 0.25% (w/v). The solution of fluorophore was prepared by dissolving 70 mg of rhodamine B (Merck) in 1000 mL of distilled water. This solution contained 0.05% (w/v) of polyvinyl alcohol (30–70 kDa, Sigma). A standard reference material from the National Institute of Standards and Technology (NIST) – SRM 2711 (Montana Soil) and a surface agricultural soil in Mallorca (Spain) were selected to study the reliability of the hybrid microcolumn-based flow system and validate the FPEDD detection method. Prior to chemical analysis, the soil was oven-dried at 105 °C until constant weight and 2-mm sieved. Soil pH was measured in 0.01 mol/L CaCl_2 at a soil to solution ratio of 1:5 (w:v) after 2 h of equilibration using a combined pH electrode as specified by ISO 10390 [40]. The pH value was 7.52 ± 0.03 . The total organic carbon (TOC) contents of 8.55% were determined by dry combustion at 900 °C after removal of carbonates with a few drops of a 20% (v/v) HCl solution. Particle size distribution of the fraction < 2 mm for determination of soil texture was performed with the Bouyoucos hydrometer method (ASTM type 152H) [41]. The agricultural soil consisting of 51.1% sand (0.05–2.0 mm), 34.5% silt (2–50 μm), and 14.4% clay (< 2 μm) was classified as loam soil.

2.2. Flow system

The hybrid flow system for in-line sequential extraction (fractionation) and automatic determination of orthophosphate in soil samples is depicted in Fig. 1. This integrated Sequential Injection (SI)/Flow Injection (FI) system is a combination of a microSIA setup (FIALab Instruments, Seattle, US) furnished with a syringe pump and a 6-port multiposition selection valve (SV), controlled by its own software (FIALab Instruments), with a dedicated secondary FI system incorporating a peristaltic pump (Minipuls 3, Gilson, Middleton, Wisconsin), a rotary injection valve (IDEX V-1451-DC, Upchurch scientific, Oak Harbor, Washington) and a solenoid valve (Parker Hannifin, Cleveland, Ohio). All components of the FI system are controlled by contact

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