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Method development based on all injection analysis for the determination of phosphorus in soil and sediment extracts

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Abstract

In this work, we have modified the technique of all injection analysis (AIA) by changing the position of the detector. The detection is then located as a part of the circulatory loop. With this new detector position, we could monitor for many numbers of circulation. The sensitivity was improved by using the cumulative signal data obtained when the number of circulation rounds was increased. The dilution effect using this new detector location was also less than that with the previous system. We employed a four-channel peristaltic pump to aspirate four types of liquids into the system together at one time. The AIA method was then developed for determination of phosphorus in soils and sediment extracts. The method was optimized for the new harmonized scheme of extraction that has been developed by the European Commission.
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1. Introduction

In dealing with large numbers of samples, use of automation methods is often worthy of consideration. For automation nowadays, flow-based techniques, such as flow injection analysis (FIA) [1] and sequential injection analysis (SIA) [2] are mostly employed. These techniques were developed to serve a variety of automated analytical applications. FIA is usually based on an injection of a liquid sample into continuous flowing streams of reagents followed by detection. In this procedure, reagents are continuously pumped to waste. On the other hand, SIA utilizes a selection valve with appropriately written software to control the valve's position for aspirating, one at a time, small plugs of either sample or reagent. The liquid plugs are held in a holding coil before being propelled into the mixing coil, and finally to the detector. In this way, consumption of reagents and samples in SIA is markedly lower than in FIA.

All injection (AI) or all injection analysis (AIA) is also a flow-based technique that was first invented by Itabashi et al. in 2001 [3]. In AIA, plugs of sample and reagents are loaded into tubular loops, which are fitted with six-way valves. These loops can either be made to be kept separated from one another or be connected by switching the valves' position. In the connecting position, the solutions can be circulated for a defined time inside the flow path. In this circulation process, the degrees of mixing and reaction are promoted due to the effect of laminar flow. Detection of signals occurs at the detector that is placed before the waste.

AIA technique is similar to SIA technique in that the plugs of all the liquids are rested inside the flow channel, before applying the main channel flow for mixing and finally detection. However, aspiration of liquid zones in AIA technique can be carried out all at once with use of the six-way valves. Zone loadings in the SIA technique are made through a selection valve and, therefore, the loading or aspiration can only be done one at a time.

We are interested in adopting the AIA technique for method development in chemical analysis. In this work, a method development for quantitative analysis of phosphorus in soil extracts is described. The method should be useful and suitable for analysis of phosphorus in the extraction protocol recently presented by representatives (Ruban et al. [4]) of the European Commission (EC). This protocol for phosphorus analysis was developed through the Standards, Measurements and Testing (SMT) program and therefore is known as the SMT protocol.

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The SMT protocol [4] involves sequential extraction of soils and sediments. Usually in a sequential extraction, there are large numbers of soils and sediment extracts to be analyzed. Thus, it would be very useful to have automated methods of analysis to support the protocol.

This paper describes a method development, based on the AIA technique using molybdenum blue method [5] for the colorimetric determination of phosphorus in soils and sediment extracts. We adopted the original AIA technique [3] and included improvements to the technique by rearranging Itabashi's manifold as well as by making the system fully automated. Our development focused on the analysis of two kinds of extractable phosphorus (P) of the SMT protocol, namely, '*NaOH extractable P*' (P bound to Al, Fe and Mn oxides and hydroxides) and '*HCl extractable P*' (P associated with Ca) [4].

2. Experimental

2.1. Chemicals and glassware

All chemicals used in this work were analytical reagent grade. Deionized-distilled water was used throughout and was directly obtained from a Milli-Q system (Millipore, USA). All glassware and low-density polyethylene containers were cleaned with the phosphate-free detergent TEEPOL (Sherwood Co. Ltd., Thailand). Rinsing was carried out using deionized-distilled water.

2.2. Soils and sediments

2.2.1. Certified reference materials
Two certified reference materials (CRMs) were purchased from the National Institute of Standards and Technology (NIST), USA. SRM 2704 is sediment from the Buffalo River, New York (particle size 38–150 μm). SRM 2711 is soil (particle size <74 μm) from Montana, USA. One other CRM, PACS-2, was purchased from the National Research Council (NRCC), Canada. PACS-2 is a standard sediment from the harbor of Esquimalt (particle size <125 μm).

2.2.2. Samples
Fifteen soil samples, collected from different agricultural areas in Thailand, were used in the method validation, as well as nine sediment samples. The soils were prepared and provided by the Soil Science Division, Department of Agriculture, Bangkok, Thailand. The sediments were collected from prawn-farming ponds. Generally, the soils and sediments were spread on polyethylene-lined trays and were left to air dry at room temperature (30 °C). The samples were gently ground to pass a 2 mm screen. Each batch of sample was then mixed for homogeneity by a process of rolling or turning.

2.3. Extracts using the SMT protocol

In our method development, there were two types of extracts based on the SMT protocol [4]. These extracts were different in the initial pH of the extractants. One type of the extracts was NaOH extractable P ('*NaOH-P*'). The sample (0.2 g) was

extracted with a base solution (1 M NaOH). The pH of this '*NaOH-P extract*' was adjusted to neutral with 3.5 M HCl and then was filtered to remove the colloid residue. The other type of extract was HCl extractable P ('*HCl-P*'). The soil or sediment residue from the first extraction step (with 1 M NaOH) was further extracted with an acid solution (1 M HCl). The '*HCl-P extract*' is normally quite acidic (pH ∼0–0.5). Details of the extraction protocol for these two types of fractions can be found in [4].

2.4. Digestion of sample and residue

Soils and sediment samples were digested for quantitative analysis of total phosphorus content. The results were used in the validation of our method. The residues left over after the extraction were also digested for residual phosphorus content (residual P).

The digestion of samples and residues were performed using a Milestone microwave (model MLS-1200 Mega, Italy). Sample or the remaining residue (oven dried at 50 °C) was placed in tetrafluormethaxil vessel. To the vessel were added 1 mL of concentrated hydrofluoric acid, 1 mL of concentrated nitric acid and 2.5 mL of concentrated perchloric acid. The vessel was fitted with a tetrafluormethaxil stopper and placed in the microwave for 30 min. During the 30 min period the power was varied every 5 min as follows: 250/400/500/500/600 W. After cooling, the clear sample solution was weighed in an analytical balance. The solution was transferred by rinsing with deionized-distilled water and made up to 25.00 mL. Phosphorus content in the digested solution was determined by a modified molybdenum blue method [6] or by inductively coupled plasma-optical emission spectrometer (ICP-OES) (Spectro ICP-OES model CIROS^{CCD}, Germany).

2.5. Automated AIA manifold

2.5.1. Apparatus
Fig. 1 shows the set up of our AIA manifold. The optimum condition for determination of phosphorus (orthophosphate) in the '*NaOH-P*' and the '*HCl-P*' extracts is described in the caption.

Six-way valves (V_1–V_5) are Rheodyne injection valves (model 5020, USA). These valves were connected, as shown in Fig. 1, without the usual injection loops fitted on them. P_1 is an Ismatic peristaltic pump (model IS7610, Switzerland) and P_2 is also an Ismatic peristaltic pump (model MS-CA 4/620, Switzerland). Detector (D) is a Jenway spectrometer (model 6450, UK).

Labview^{TM} 6.1 was employed to computerize the AIA manifold. The software was used to control pumps (P_1 and P_2) and valves (V_1–V_6) to work synchronously.

2.5.2. Carrier
The carrier (C) in Fig. 1 depended on the type of extracts. We prepared two types of carriers, '*NaOH-P carrier*' and '*HCl-P carrier*'. These carriers were prepared to make the matrices as closely as possible to the matrices of the sample extracts from the SMT protocol. The '*NaOH-P carrier*' was used when we
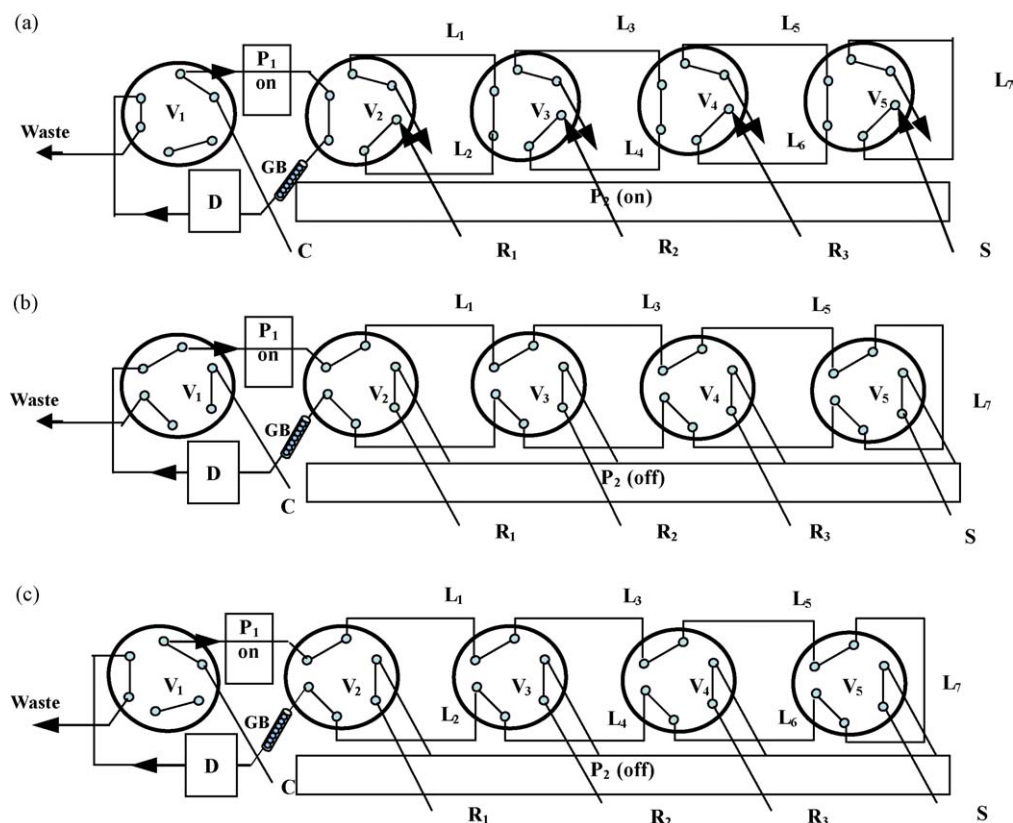
Fig. 1. Schematic diagram of the AIA system (optimum condition). (a) 'Loading step': carrier (C), sample (S) and reagents (R_1–R_3) are loaded into the loops (L_1–L_7); (b) 'circulation step': all loops are connected by switching all the valves from 'load' to 'inject' positions, and the reaction mixture is circulated before being introduced into the detector; (c) 'washing step': the reaction mixture is flushed to waste by switching V_1 to 'load' position. V_1–V_5: six-way valves. P_1 and P_2: peristaltic pumps operating at 4.2 and 1.6 ml/min, respectively. D: spectrometric detector (690 nm), fitted with 5 cm flow cell. GB: Tygon tube (3.0 mm × 55 mm), packed with glass beads (3 mm, o.d.). R_1: tin(II) chloride 1.2 g/L + hydrazine dichloride 1 g/L, in 0.5 M H_2SO_4. R_2: ammonium molybdate 12 g/L in 0.3 M H_2SO_4 (for '*NaOH-P*') and in 0.6 M H_2SO_4 (for '*HCl-P*'). R_3: tartaric acid 2.4 g/L. L_1–L_6 and L_7 are PTFE tubes (0.5 mm, i.d.) with lengths of 15 cm and 20 cm, respectively. The carriers (C) are selectable between the carrier for '*NaOH-P*' analysis and for '*HCl-P*' analysis.

determined phosphorus content in the '*NaOH-P*' extracts and '*HCl-P carrier*' for determination of phosphorus in the '*HCl-P*' extracts. To prepare the '*NaOH-P carrier*', 400 mL of 0.7 M NaOH were mixed with 400 mL of 1 M HCl. Water was added to this mixture to make 1 L. The '*HCl-P carrier*' is simply a solution of 1 M HCl.

2.5.3. Operating procedure

The steps of operation are summarized in Table 1. Typically, there are three operational steps in our AIA system. Table 1a

presents the full procedure, consisting of the steps for 'loading', 'circulation' and 'washing'. The procedure in Table 1a is suitable when we want to circulate the liquid plugs (after loadings) for more than one cycle. The following describes all the steps listed in Table 1a.

'Loading': All reagents and the sample solution are loaded into the loops (L_1–L_7), fitted on valves V_2–V_4 (for reagents) and V_5 (for sample/standard). This is performed using the peristaltic pump P_2. V_1 is filled with the carrier using the peristaltic pump P_1.

Table 1
Operational steps for the AIA manifold shown in Fig. 1

Step	V_1 (carrier)	V_2 (tin (II) chloride)	V_3 (ammonium molybdate)	V_4 (tartaric acid)	V_5 (sample/ standard)	P_1	P_2	Duration time (s)
(a) Operational steps for >1 circulation								
1. Loading	Load	Load	Load	Load	Load	On	On	10
2. Circulation	Inject	Inject	Inject	Inject	Inject	On	Off	$25 \times n$[a]
3. Washing	Load	Inject	Inject	Inject	Inject	On	Off	40
(b) Operational steps for 1 circulation								
1. Loading	Load	Load	Load	Load	Load	On	On	10
2. Circulation + washing	Load	Inject	Inject	Inject	Inject	On	Off	40

[a] *n*: The desired circulation round.

'Circulation': All valves are switched to 'inject' positions and P_1 and P_2 are switched to the 'on' and 'off' mode, respectively. This allows the liquids to travel clockwise. The duration in this step can be varied to obtain the desired number of rounds of circulation. We count the number of circulation each time the signal rises (indicating that the sample zone is passing the detector). For example, we would obtain consecutive four signal readings when the duration time, in the 'circulation' step, is adjusted to 100 s (Table 1a).

'Washing': When the signal is adequately obtained to the desired number of circulation rounds, valve V_1 is switched to the 'load' position. This allows all the liquid inside the system to travel past the detector and finally to the waste.

If the sensitivity is not critical, calibration can be done using only the data obtained from the first circulation. For one circulation procedure, the operational steps are described in Table 1b.

3. Results and discussion

3.1. Improvements on the original AIA technique

The improvements to the original AIA technique of Itabashi et al. [3] are summarized in Fig. 2.

3.2. Employment of peristaltic pumps

We replaced the double-plunger pump in Fig. 2a with a much cheaper peristaltic pump (Fig. 2b). A peristaltic pump is usually available in laboratories working with flow analysis. A peristaltic pump is more versatile than the double-plunger pump, and pulsation of the flow, driven by the rollers in peristaltic pump, may contribute to a better mixing of the liquid plugs. Mixing would be poorer with a lower pulsation pump.

The original manifold [3] employed four syringes for filling the sample and reagents (Fig. 2a). A peristaltic pump can be used instead of the syringes. As shown in Fig. 2b, we used a second peristaltic pump (P_2) that is capable of pumping four channels of liquid. In this way, we were able to control the filling and rinsing of every reagent, just by turning the pump (P_2) on or off. Analysis by the modified AIA method was therefore more rapid.

3.3. Automation

With these changes made to the AIA system, it was very simple to computerize the system. Through a small controlling box (Fig. 2b), we could send commands to turn the pumps (P_1 and P_2) to either 'on' or 'off' position. We could also control valves (V_1–V_5) through the same box to either the 'load' or the 'inject' position (Fig. 1). Recording of signal started automatically once the liquid inside the main channel starts to flow. Our AIA can be coupled with an auto-sampler to make a completely automated system.

3.4. Benefits from changing detector position

We have changed the detector's position by placing it closer to V_2 (Fig. 2). With this simple modification, we have gained the following advantages.
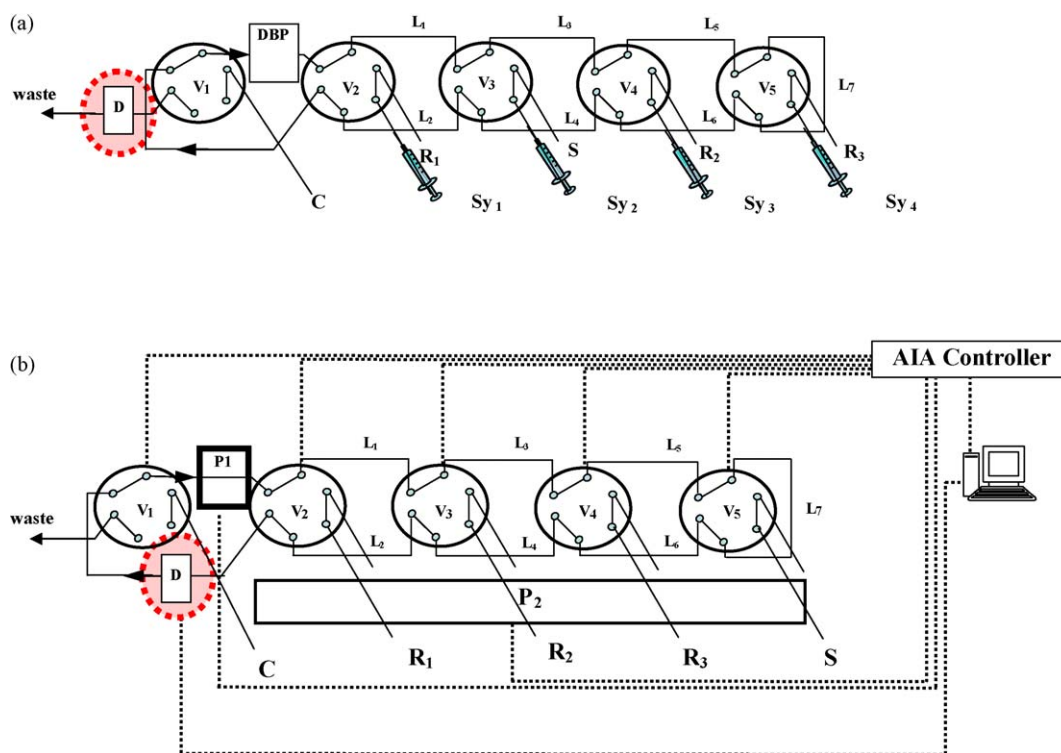

Fig. 2. Changes made to Itabashi's AIA to improve analytical features. There was a change in position of detector (D) and the employment of a second peristaltic pump (P_2) to replace the four syringes (Sy_1–Sy_4). R_1–R_3 represent reagents required for the chemical analysis. C is a suitable carrier. V_1–V_5 are six-way valves, fitted with PTFE tubes, L_1–L_7. DBP is a double-plunger pump and P_1 is a peristaltic pump.

Table 2
Improvement in sensitivity by our modification of Itabashi's system

Type of AIA manifold	Calibration curve from molybdynum blue method ('NaOH-P')	Calibration curve from dye solutions	Dispersion coefficient[b]
a. Itabashi's manifold (Fig. 2a)	$A = 0.241[P] - 0.010$; $r^2 = 0.998$	$A = 0.410[dye] - 0.009$; $r^2 = 0.997$	9.61
b. Our manifold[a] (Fig. 2b)	$A = 0.302[P] + 0.009$; $r^2 = 0.997$	$A = 0.509[dye] + 0.004$; $r^2 = 0.999$	7.69

[a] Results are from the first circulation only.

[b] The dispersion coefficient was determined as described by Ruzicka and Hansen [1].

3.5. Options for desired dilution

In FIA, we often vary the length of mixing coil to find an optimum condition in which an appropriate sensitivity is achieved. In the usual cases, we tend to optimize for the highest sensitivity. In colorimetric methods, a too long reaction coil or mixing coil will cause large dilution effect of the color product. However, there are some cases where sample dilution is necessary.

With the new position of detector in our manifold (Fig. 2b), the sensitivity for phosphate (Table 2) was improved. The slope obtained from our manifold was greater than the slope obtained from Itabashi's manifold. To prove that this was the effect from the decrease in dilution, a further experiment was carried out using a blue dye.

A series of aqueous dye solutions was aspirated into L_7, for both the systems shown in Fig. 2. The rest of the flow channels (including L_1–L_6) were filled with water. In Table 2, the slopes from the dye experiment together with the dispersion coefficients show that the manifold in Fig. 2b gave a smaller dilution than the manifold in Fig. 2a. Hence, we concluded that the rearrangement of the detector's position is an option to improve sensitivity.

In some applications, samples may contain rather high concentrations of the analytes. In these cases, pre-dilution of samples before analysis is needed.

If we operate the modified AIA system in Fig. 2b by using the operation procedure in Table 1a, we were able to circulate the solution inside the AIA system. The number of circulation could be varied. Fig. 3a shows an example of the signals obtained from three cycles. The signal obtained from the first circulation is the highest because it was the least diluted. This characteristic offers us the choice of using either or all of the signals to construct the calibration, as well as to compromise for the desired sensitivity. If the first signal is too high or off-scale, we can select to use the signal from the second circulation and neglect the one from the first circulation. In this way, pre-dilution is not necessary.

3.6. Options for making calibration curve

The rearrangement of the detector's position (Fig. 2) also offers other options in the creation of the standard curves. Fig. 3b illustrates another procedure to improve the sensitivity (slope) of the calibration. The signals obtained from at least two circulations were summed up together to increase the slope of the standard curve.

3.7. Signal characteristics

AIA often produces a blank signal. Fig. 4 exemplifies that, in the same signal profile, there are both negative and positive sides. The blank reading and negative readings are caused by dissimilarity in the refractive indices of the liquid plugs in the main flow channel of AIA. In our manifold shown in Fig. 1, the refractive indices were 1.3387 (for carrier), 1.3365 (for R_1), 1.3359 (for R_2), 1.3301 (for R_3) and 1.3388 (for a standard solution).

To operate a blank injection, the carrier was aspirated into the loop L_7, via the 'S' position (Fig. 1). There was practically no orthophosphate inside the system and therefore no colored product was produced. Nevertheless, the blank signals (Fig. 4) were relatively high compared to normal blank signals in the FIA technique. These significant readings of the blank were due to the effects of refractive index [7,8], which are unavoidable in the AIA technique.

One other phenomenon that can quite clearly be observed in the AIA technique is the negativeness of the profiles. This is also an unavoidable consequence from the refractive index effect, which can enhance either the focusing or the straying of light entering the photodiode.
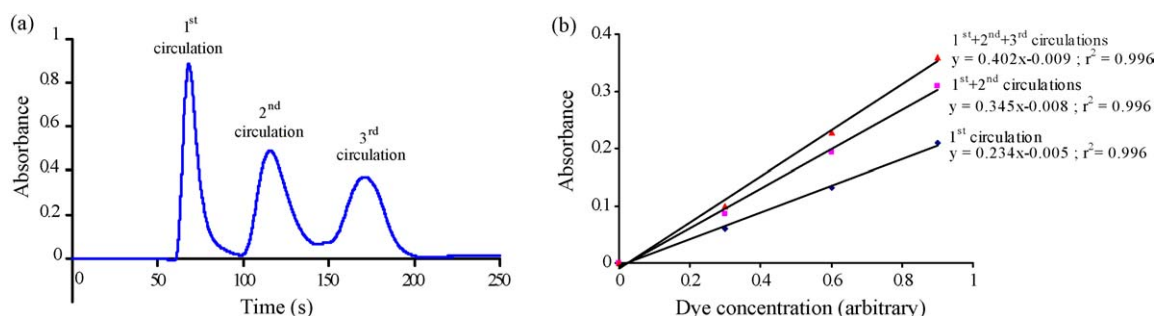

Fig. 3. Benefits from changing the detector's position. (a) Allowance in selection for appropriate signals from any circulation round; and (b) increased sensitivity by summation of signals from at least two circulations. The results were obtained from injections of blue dye solutions into the AIA set up shown in Fig. 1.
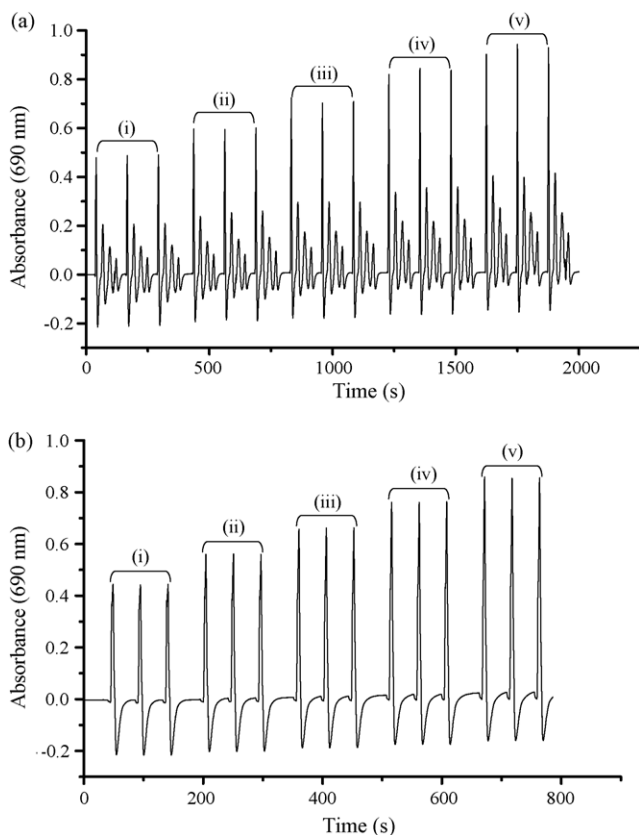
Fig. 4. AIA profiles in the analysis of phosphorus. (a) Four circulations and (b) one circulation. The results were from triplicate injections of: (i) blank; (ii) 0.2 mg P/L; (iii) 0.4 mg P/L; (iv) 0.6 mg P/L; and (v) 0.8 mg P/L.

These uncharacteristically high blank and partial negative signals are not commonly seen in FIA technique. In FIA, it is quite easy to prevent them just by making a good matrix matching between the sample and the carrier [7].

3.8. Optimization for analysis of phosphorus

This work focused on method development for the determination of phosphorus in '*NaOH-P*' and '*HCl-P*' from the SMT protocol. The concentrations of reagents (R_1–R_3) were taken from our preliminary studies carried out in FIA [9]. We paid particular attention to the optimization of the following physical parameters.

3.9. Sequence of reagent and tolerance limit for silicate

Firstly, we concentrated on the tolerance limit towards silicate, which is the most potential source of interference in the quantitative analysis of phosphate by the molybdenum blue method [10–13].

We investigated two arrangements of the sequence of liquid zones as depicted in Fig. 5. Fig. 5a and Fig. 5b schematically represents two sequence patterns in the 'circulation' step of Fig. 1. Relationship of sequence and tolerance in the analysis of '*NaOH-P*' was studied.

In Fig. 5a, the sample plug was directly in contact with the molybdate solution, whereas in Fig. 5b, tartaric acid, which is the masking reagent for silicate [14], was placed between the zones of molybdate solution and the sample. The results, indicated in Fig. 5, showed that the sequence in Fig. 5a had a better sensitivity than the sequence in Fig. 5b. However, the system in Fig. 5b, with tartaric acid as the masking agent, gave a better tolerance limit for silicate.

For further optimization studies, the sequence depicted in Fig. 5b was chosen.

3.10. Appropriate sample volume

In our AIA system, the volume of sample is determined by the length of the loop L_7. The results taken from the system of
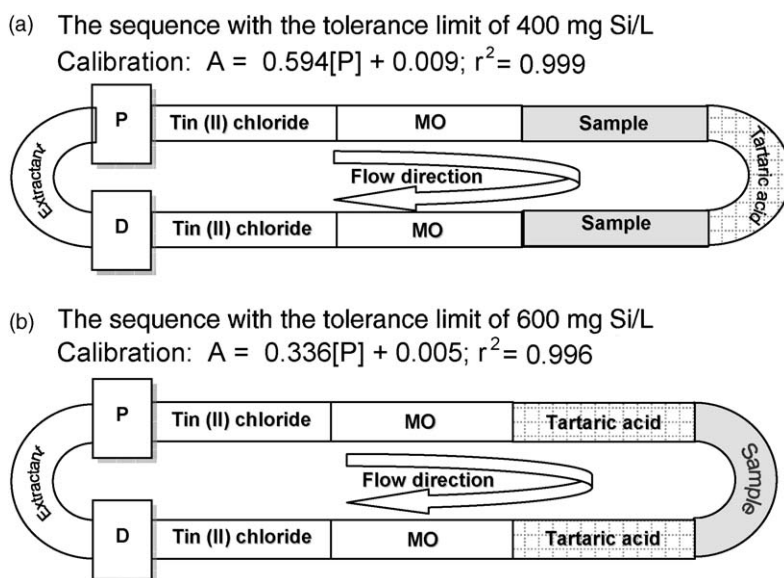

Fig. 5. Schematic diagram of the AIA flow paths. The reported limits are for '*NaOH-P*' analysis, which were obtained by addition of silicate standards (0–1200 mg Si/L) into 0.6 mg P/L of standard phosphate. Alteration within the range of 3S.D. of the signal, obtained from the phosphate standard, is considered to be tolerant of interference from silicate. MO: ammonium molybdate reagent, P: pump, D: detector.

Table 3
Effect of sample volume on calibration and signal profile (volumes of other reagents were fixed at 120 μL)

Sample volume (μL)	Calibration; r^2 (for 0.3–0.9 mg P/L)	Signal shape (first circulation)
60	$A = 0.339[P] - 0.001; r^2 = 0.999$	Singlet
80	$A = 0.521[P] + 0.011; r^2 = 0.996$	Singlet
100	$A = 0.533[P] - 0.004; r^2 = 0.999$	Singlet
150	$A = 0.729[P] - 0.003; r^2 = 0.999$	Doublet
250	$A = 0.793[P] + 0.007; r^2 = 0.999$	Doublet

'*NaOH-P*' are shown in Table 3. As expected, the sensitivity was improved by increasing the size of sample. However, mixing was less efficient when the sample size was greater than 100 μL. As shown in Table 3, sample volumes of 150 and 250 μL gave doublet shape of profiles. Thus, there was an optimal sample zone, although we noticed that the effect of zone length decreased with increase in the number of circulation.

3.11. Analytical features

The performance of the AIA method developed for detection of phosphorus in soils and sediment extracts is presented in Table 4. Compared to the FIA technique, our AIA method dispensed about three times less reagents in the analysis of a sample. The throughputs and precisions were comparable to those of FIA. As indicated in Table 4, the working range and detection limits were appropriate for this application of the SMT protocol for soils and sediment extracts. The system was more sensitive in the '*NaOH-P*' than in the '*HCl-P*' medium.

The tolerance for silicate at 600 mg Si/L is adequate in the analysis of '*NaOH-P*'. The toleration in the '*HCl-P*' analysis was not determined, because solid crystals of sodium metasilicate (used as silicate standard) were sparingly soluble in the '*HCl-P*' extractant. It is therefore very unlikely that this type of interference is present in the '*HCl-P extract*' [4].

3.12. Method validation

Two attempts were made to validate the AIA method (Fig. 1). Sequential extraction of the SMT protocol for '*NaOH-P*' and

Table 4
Performance of our AIA method developed for the analysis of phosphorus in the SMT protocol

Analytical feature	AIA method for	
	'*NaOH-P*'	'*HCl-P*'
1. Reagent/sample consumption (μL)	≤1000	
2. Sensitivity (slope)	0.534	0.335
3. Working range (mg P/L)		
4. Sample throughput (samples/h)	0.0–1.0	
	72	
5. Level of precision (R.S.D.)	0.19–0.36	0.16–0.29
6. Limit of detection[a] (mg P/L)	0.02	0.04
7. Silicate interference (mg Si/L)	600	–[b]

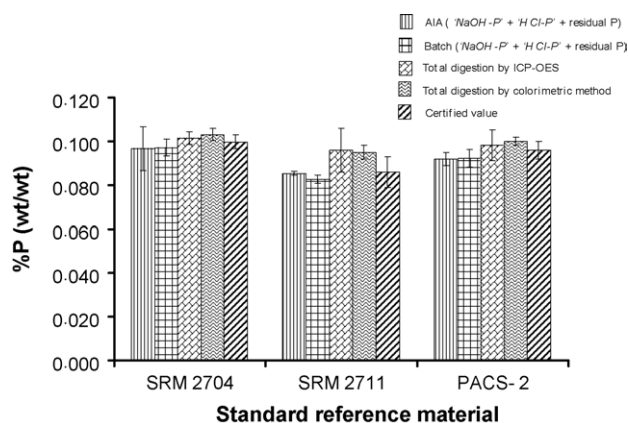[a] 3S.D./slope.
[b] Not determined.

Fig. 6. Comparison of phosphorus content determined by SMT protocol (AIA and batch) and by total digestion (ICP-OES and colorimetric method) of three certified reference materials with certified values.

'*HCl-P*' [4] were applied to three CRMs and 24 samples of soils and sediments.

3.13. Using CRM

For the CRMs, we extracted the reference materials, followed by digestion of the material residues. Three kinds of fractions were obtained: (a) '*NaOH-P*'; (b) '*HCl-P*'; and (c) digested residue (residual P). The first two fractions were analyzed by our AIA method and by the traditional molybdenum blue method [6]. The digested residue was analyzed by ICP-OES. The contents in these three fractions were combined to obtain the total phosphorus content.

The total phosphorus contents of CRMs were also determined by digestion (but without any extraction). CRMs were digested by the method used for the residues. After digestion, determination of phosphorus was carried out using ICP-OES and the conventional molybdenum blue batch method [6].

Results of these experiments are shown in Fig. 6. No significant difference (ANOVA test at 95% confidence limit [15]) was found amongst the results ($F_{experiment} = 1.51$ and $F_{critical} = 3.48$).

3.14. Using soils and sediment samples

Sequential extractions for '*NaOH-P*' and '*HCl-P*' were carried out on 15 soils and nine sediment samples. Analysis of residual P (phosphorus content in the extraction residues was not performed.

The phosphorus contents in the '*NaOH-P*' and '*HCl-P*' fractions were determined by our AIA method and compared with the conventional molybdenum blue batch method [6]. According to paired *t*-test [15], there was no significant difference at 95% confidence level ($t_{observed} = 0.44$ and $t_{critical} = 1.71$).

4. Conclusion

This work demonstrated progressive improvements that were made to the original AIA technique. The detector was reallocated

as part of the main flow loop, and this has markedly brought about quite a few alternatives to the technique. The developed system offers automatic control of all the pumps, valves and automatic start of signal recording.

We observed that the effect of refractive index, the Schlieren effect [7], can be quite significant and may be difficult to avoid in the AIA technique. This has resulted in a negative signal as well as giving a reading from a reagent blank.

An AIA method for quantitative analysis of phosphorus was developed in this study. Some results demonstrated that we should pay attention to the selection of the sequence of reagents in AIA to avoid having common serious interference effect from silicate. The phosphate method was validated for extracts of soils and sediments using a standardized protocol, presented recently by the European Commission.

Acknowledgement

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