Multi-syringe flow injection system with in-line microwave digestion for the determination of phosphorus

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Abstract

A multi-syringe system for spectrophotometric determination of total phosphorus involving in-line digestion is proposed. Sample and digestion solution were dispensed and directed towards a digestion vessel located inside a domestic microwave oven (MWO) where sample digestion took place. Afterwards, the digested sample was merged with the necessary reagents for the colorimetric determination based on the molybdenum blue method. Several digestion conditions were studied regarding composition of digestion solution, digestion time and power set on the MWO. The system was applied to waste water samples and results shown a good agreement with the reference method. Repeatable results (R.S.D. $< 2.41\%$) and determination frequency of $12\,h^{-1}$ were obtained.

Introduction

The flow injection analysis (FIA) concept introduced in the middle 70s [1] together with the sequential injection analysis (SIA) approach presented in the 90s [2] produced a dramatic increase in the interest of analytical chemists in flow analysis, both in terms of application to different matrices and also to the proposal of new ways of in-line sample manipulation. Actually, techniques and equipment have been recently described to improve relevant aspects in flow analysis like sample/reagent(s) interaction, extension of automation, multi-analyte determination with the same manifold configuration, flow reproducibility, ability to efficiently carry out separation processes, or even to make complex digestion of the samples. Among these recently proposed techniques, the multi-commutation concept [3] associated with the multi-syringe [4] apparatus provides the possibility to establish different sample pathways and to assure a very stable and reproducible flow-rate in up to four different channels.

Microwave (MW) sample preparation is becoming established as the sample preparation technique of choice due to its efficiency, relatively low cost and robustness. A new understanding of reaction-enhancing in the field of environmental analysis marked the broad applicability of this technique [5]. On the other hand, coupling MW sample preparation with flow analysis can enhance sample throughput and lower consumption of sample and/or reagents, allowing the development of procedures which are simple, relatively safe and applicable to samples of different nature [6,7]. Nevertheless, the association of these analytical tools can be limited by formation of gas bubbles during the digestion step, which can compromise the determination results, especially when spectrophotometric detection is concerned.

SIA systems bearing this type of digestion have also been described [8–11]. All manifolds included a digestion chamber, placed in a lateral port of the selection valve. This approach avoided bubble introduction into the flow system, as the digestion chamber content was only partially aspirated for further determination/detection.

In the present work, the possibilities offered by FIA and SIA were exploited by using a multi-syringe flow injection (MSFIA) system for implementing in-line sample treatment. The main objective was the integration of microwave digestion in a flow system that included a multi-syringe as propulsion device and solenoid valves to create a flow

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network where sample digestion and determination could be carried out. The determination of total phosphorus in water samples was chosen to illustrate the feasibility of this approach. The methodology chosen was based on the formation of phosphomolybdenum blue, performed after microwave in-line sample digestion. Flow injection systems incorporating microwave digestion before determination of total amount of phosphorus in water samples have already been reported [12–14]. The digestion was carried out in long (6, 7.2 or 7.6 m) tubular reactors with narrow inner diameter (0.5–1.0 mm), which can often originate bubble formation. Debubblers or cooling coils were adopted to circumvent their interference in the detection systems. In the present work, another strategy to avoid this problem was adopted, replacing the coil by a digestion vessel.

Experimental

2.1. Reagents and solutions

For the preparation of all solutions, water from MilliQ system was used and all chemicals were analytical reagent grade. A stock solution (1200 mg P L^{-1}) of potassium dihydrogen phosphate (Merck) was prepared by dissolving 5.27 g of the solid per liter of water. An intermediate working solution containing 60 mg P L^{-1} was prepared daily by diluting 5.00 mL of the stock solution to 100 mL. Working standards from 3.00 to 36.0 mg P L^{-1} were obtained by dilution of intermediate working solution with water. The glassware for phosphorus determination was soaked in nitric acid (1 mol L^{-1}) and rinsed with water.

A sulfuric acid stock solution (2.5 mol L^{-1}) was prepared by dilution of concentrated sulfuric acid ($d = 1.98$; 98%). Ammonium heptamolybdate tetrahydrate (100 g L^{-1}) and potassium antimony(III) oxide tartrate hemihydrate (2.74 g L^{-1}) stock solutions were prepared by dissolving 10.0 and 0.274 g in 100 mL of water, respectively. The color reagent consisted of a mixture of those stock solutions: 100 mL of sulfuric acid (2.5 mol L^{-1}), 80 mL of ammonium heptamolybdate tetrahydrate (100 g L^{-1}) and 7.3 mL of potassium antimony(III) oxide tartrate hemihydrate (2.74 g L^{-1}) were mixed and the volume was made up to 500 mL with water. The ascorbic acid solution (reducing reagent) was obtained by dissolving 0.81 g of ascorbic acid in 500 mL of water. Both color and reducing reagents were prepared daily. Water was used as carrier solution. The digestion solution consisted of a mixture of 0.4 mol L^{-1} sulfuric acid and 24.5 g L^{-1} potassium peroxodisulfate.

Several inorganic and organic phosphorus standards (12 mg P L^{-1}) were prepared to test the efficiency of the digestion. They were obtained by dilution of aqueous stock solutions (1.2 g P L^{-1}) of sodium phenylphosphate, D-glucose 6-phosphate, sodium diphosphate decahydrate, and phytic acid dipotassium salt, prepared by dissolving 0.984, 1.18, 0.864, and 0.475 g of the solid in 100 mL of water, respectively. The stock solutions of sodium triphosphate hexahydrate and adenosine 5′-triphosphate (1.2 g P L^{-1}) were prepared by weighing 0.123 and 0.142 g, before dissolving each solid separately in 20 mL of water. A sodium trimethylphosphate ($d = 1.214$; >98%) solution (12 mg P L^{-1}) was also prepared by diluting 5.43 to 100 mL in water.

2.2. Apparatus

Solutions were managed through the flow network by means of a multi-syringe burette (Crison Instruments, Allela, Spain). This device is a multiple channel piston pump, where all pistons are driven by a single motor of a common automatic burette. It is also controlled by computer software through a serial port. Syringes with different volume capacities can be applied simultaneously. For this application, a 5 mL syringe was placed in position 1. Ten milliliter syringes were placed in the other positions. A three-way commutation valve (NResearch, Caldwell, NJ, USA) was connected to the head of each syringe and four extra commutation valves were included in the module used. For all valves, the exchange options were classified in on/off lines. The “on” line was assigned to the solution flasks and the “off” line was reserved for the flow network.

A personal computer (Samsung SD 700) equipped with an Advantec (Taipei, Taiwan) PCL818L interface card, running a lab-made software written in QuickBasic 4.5 (Microsoft), controlled the multi-syringe operation (piston movement and position of solenoid valves) and peristaltic pump activation.

As detection system, a Thermo-Spectronic (Cambridge, UK) Heλios γ UV-Vis spectrophotometer equipped with a Hellma (Mullheim/Baden, Germany) 178.712-QS flow-through cell (internal volume 18 μL) was used and the wavelength was set at 880 nm. The analytical signals were recorded in a Kipp & Zonen (Delft, The Netherlands) BD 111 strip chart recorder.

For the in-line digestion a domestic Becken MWB 1000 Microwave Oven was used with a maximum power of 700 W. A lab-made PTFE digestion vessel (Fig. 1) with a internal volume of 2.2 mL and a glass spiral with 0.73 mL of capacity was placed inside the MW oven. The vessel was connected to the system by PTFE tubing passing through the ventilation holes. The end-fittings connected to the digestion vessel were made of polypropylene (Valco, Schenkon, Switzerland) to stand high temperatures. Possible microwave radiation leakage was tested using a microwave leakage detector (Model MD-2000, Comfort House, Newark, USA). The radiation volume measured during operation did not exceed 5.0 mW cm^{-2}.

2.3. Manifold

The system components were disposed as shown schematically in Fig. 2. All connections were made of PTFE tubing (0.8 mm i.d.) with Gilson (Villiers-le-Bel, France)

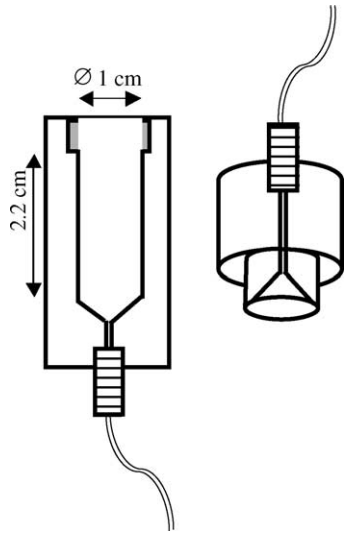

Fig. 1. Schematic representation of the digestion vessel.

end-fittings and connectors, except the reaction coil tube that was made from FEP tubing (0.8 mm i.d.) as its characteristics (more rigid and slightly less porous than PTFE) minimised the retention of molybdenum blue-colored complex in tube walls. All tubing were purchased from Omnifit (Cambridge, UK). A Gilson Minipuls 3 peristaltic pump equipped with PVC tubing was used to propel air or water through the digestion vessel.

The holding coil (HC) and the reaction coil (RC) were 400 and 100 cm long, respectively. The tubing length between valve V7 and confluence X1 was 10 cm. The connection between this confluence and the digestion vessel was 83 cm long. The tubing connections signed in Fig. 2 as L1–L4 were 18, 12, 10, and 10 cm long.

2.4. Procedure

The protocol sequence is given in Table 1. This procedure included three parts: in-line microwave digestion, colorimetric determination, and washing of the system.

The first two steps of the operating sequence consisted of filling L1 tube with a new sample, eliminating the excess through waste. Then, 0.350 mL of sample were aspirated towards the HC. After that, 0.800 mL of the solution kept in the HC and 0.400 mL of digestion solution were mixed in X1 and propelled to the digestion vessel. Subsequently, air was introduced into the connection between X1 and digestion vessel using a peristaltic pump, resulting that the sample zone was placed in the vessel between two air zones. The digestion was carried out during step F: the MW oven was switched on during 30 s with the power set at 595 W. Meanwhile, tubes L2–L4 were washed with water delivered by syringe 2. During digestion, a beaker containing 200 mL of water was placed inside the MW oven, to absorb the excess of the radiation.

After digestion, the vessel content was drawn by the peristaltic pump until it reached confluence X1, followed by its aspiration by syringe 2 to the HC. The digested sample was dispensed through confluence X2, followed by elimination

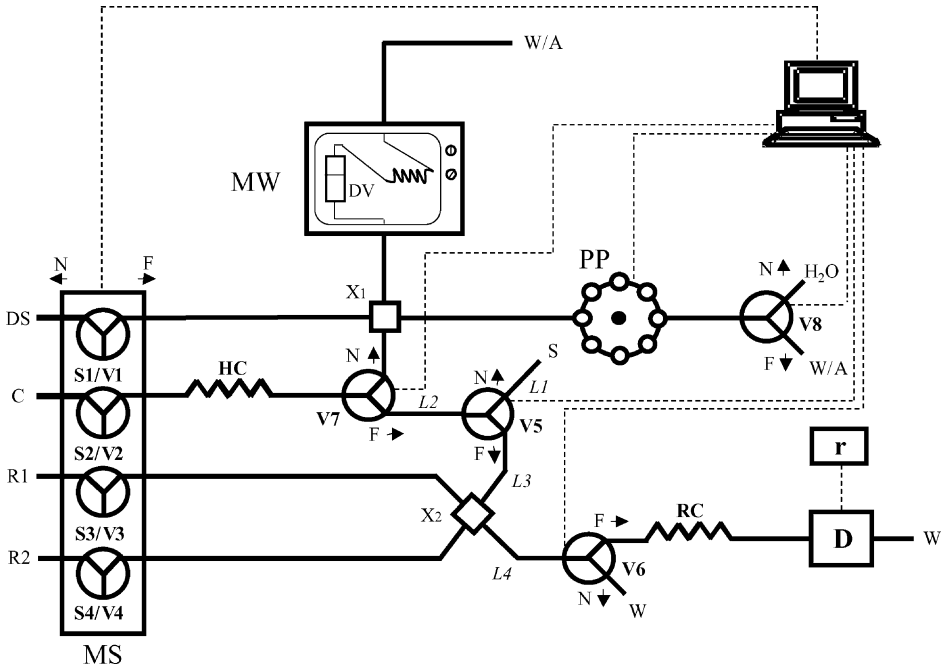

Fig. 2. MSFIA system for the determination of total phosphorus with in-line microwave digestion: MS, multi-syringe; S*i*, syringe; V*i*, solenoid valves; N, on position; F, off position; MW, microwave oven; DV, digestion vessel plus glass spiral; PP, peristaltic pump; HC, holding coil; RC, reaction coil; D, detector; r, recorder; X, confluences; L, PTFE connections; S, sample; DS, digestion solution; C, carrier (water); R1, color reagent; R2, reducing reagent; W, waste; and A, air.

Table 1
Protocol sequence for the determination of total phosphorus

Step	Volume (mL)	Flow rate (mL min^{-1})	Operation	Position of solenoid valves								Peristaltic pump[a]	Description
				V1	V2	V3	V4	V5	V6	V7	V8		
A	0.200	5.0	Pick up	N	F	N	N	N	F	F	F	–	Fill tube L1 with sample
B	0.600	5.0	Dispense	N	F	N	N	F	N	F	F	–	Wash tube L2
C	0.350	5.0	Pick up	N	F	N	N	N	F	F	F	–	Sample aspiration
D	0.800	4.0	Dispense	F	F	N	N	F	F	N	F	–	Send sample and digestion solution to the MWO
E	0.075	1.0	Wait	F	F	F	F	F	F	F	F	Propel	Pump air to push the mixture to the digestion vessel
F	1.250	2.5	Dispense	N	F	N	N	F	N	F	F	–	Digestion during 30 s and wash of tubes L2–L4
G	0.080	1.0	Wait	F	F	F	F	F	F	F	F	Aspirate	Aspirate air from the tubing connected to digestion vessel
H	1.150	3.0	Pick up	N	F	N	N	F	F	N	F	–	Aspirate the digested sample through the holding coil
I	0.300	5.0	Dispense	N	F	N	N	F	N	F	F	–	Propel the digested sample until the confluence X_2
J	0.200	5.0	Dispense	N	N	F	F	F	N	F	F	–	Wash tube L4
K	1.000	5.0	Dispense	N	N	F	F	F	F	F	F	–	Set the baseline
L[b]	0.150	2.0	Dispense	N	F	F	F	F	F	F	F	–	Injection of digested sample
M[b]	1.500	0.6	Dispense	N	N	F	F	F	F	F	F	–	Color reaction and signal registration
N	8.200	7.0	Pick up	N	N	N	N	F	F	F	F	–	Fill syringes
O	4.500	5.0	Dispense	N	F	N	N	F	F	N	N	Propel	Wash of the holding coil and the digestion vessel
P	1.700	2.0	Dispense	N	F	N	N	F	N	F	F	Aspirate	Wash tubes L2–L4 and aspirate water from digestion vessel
Q	2.000	5.0	Dispense	N	N	F	F	F	F	F	F	–	Set the baseline
R	7.400	7.0	Pick up	N	N	N	N	F	F	F	F	–	Fill syringes

The indicated values for flow rate and volume are referred to a 10 mL syringe. N and F represent on and off position, respectively.
[a] Flow rate at 6 mL min^{-1}.
[b] These steps were repeated three times.

of the excess present in L4 towards the waste. Before the colorimetric measurement, the baseline was set by propelling R1 and R2 to the spectrophotometer.

The colorimetric determination was achieved by dispensing 0.150 mL of digested sample together with reagents R1 and R2 towards the reaction coil. Then, both reagents were propelled to direct the reaction mixture to the spectrophotometer. These two steps (L and M) were repeated three times.

The subsequent steps corresponded to the simultaneous washing of the digestion vessel and tubes L2–L4, using both multi-syringe and peristaltic pump. After filling the syringes up to 90% of their capacity, the system is ready to begin another procedure, leaving the tubes involved in the digestion process filled with air.

3. Results and discussion

3.1. Implementation of digestion system in MSFIA

The MSFIA system was designed for carrying out in-line MW digestion based on a strategy similar to that adopted in SIA systems where sample and digestion solution are sent to a digestion vessel. After digestion, the digested sample is recovered for further determination. Hence, in the present system, the digestion vessel was connected to the flow manifold through one of its apertures and valve V7 was included to direct the sample plug towards it or into the system.

The presence of an additional pump was considered essential to allow washing of digestion vessel and tubes without resorting to multi-syringe operation. Moreover, the valve V8, connected to the peristaltic pumping tubing, allowed the selection between water reservoir or waste. In this way, the digestion vessel could be filled with water when the pump was operated in one direction or it could be totally emptied when the pump functioned in the other direction.

The inclusion of confluence X1 had two roles. Firstly, it allowed mixture of digestion solution and sample plug when these solutions were directed towards the vessel before digestion. On the other hand, the solution present in the digestion vessel could be handled through the peristaltic pump, without interference of the multi-syringe.

In multi-syringe flow systems, it is not feasible to introduce the sample into the system through one of the available syringes as it would take a long time of washing steps for avoiding carry-over effect. Hence, other devices (selection or commutation valves) must be incorporated to

the manifold to provide access to these solutions. In the present work, as the strategy chosen for sample introduction into the system was time-based, valve V5 was placed in the manifold. In this way, the volume chosen depended on the flow rate and time during which sample was aspirated into the system and its value was fixed at 0.350 mL.

The total volume introduced into the digestion vessel (step D) was varied. This volume corresponded to the sum of the volume of sample pushed by carrier (syringe 2–10 mL) and the volume of digestion solution (syringe 1–5 mL). The tested volumes were: 1.350 mL (0.900 + 0.450), 1.200 mL (0.800 + 0.400) and 1.050 mL (0.700 + 0.350), where values in parenthesis are (sample + digestion solution). The last volume was insufficient to obtain three repeatable determinations, using an injection volume (step L) of 0.150 mL. When the first volume was tried, back-flush occurred and part of the plug was lost through waste. Hence, 1.200 mL was chosen as total volume as good repeatability was achieved and no plug was lost.

3.2. MSFIA system for the determination of phosphate

As the main purpose of this work was the implementation of in-line sample digestion, concentration of sulfuric acid, ammonium heptamolybdate tetrahydrate, potassium antimony(III) oxide tartrate hemihydrate, and ascorbic acid were fixed at 0.5 mol L^{-1}, 16, 0.040, and 1.62 g L^{-1}, respectively.

The volume of digested sample for colorimetric reaction was selected aiming to perform three determinations from the same digestion cycle. As the volume drawn from the digestion vessel was limited by its size, the largest volume that could be recovered to HC without introduction of air was 1.150 mL (step H). With this value fixed, the volume of digested sample was varied up to 0.200 mL. The maximum value that provided good repeatability for three consecutive determinations was 0.150 mL. The analytical signal obtained for the third determination was lower when volumes larger than 0.150 mL were tested.

The inclusion of confluence X2 in the manifold allowed different strategies for addition of reagents to digested sample through software control, without physical reconfiguration. Two of them were tried: (A) simultaneous introduction of reagents and digested sample and (B) intercalation of digested sample between two plugs of reagents. For the second option, a double peak was registered, possibly due to insufficient mixture between sample and reagents. Additionally, sensitivity was 50% of that obtained using option A. Hence, simultaneous introduction of reagents and digested sample was chosen for further studies.

3.3. In-line microwave digestion

In order to evaluate the digestion efficiency, different digestion solutions were tested. Inorganic and organic phosphorus compounds were introduced into the system and compared to an equivalent potassium orthophosphate standard, for further calculation of the conversion percentage.

In a preliminary study, solutions of nitric acid with concentration in the range 3–7 mol L^{-1} were tried, but low conversion values were achieved for a 12 mg P L^{-1} phenylphosphate solution, keeping the MW on at 700 W during 30 s. This experiment was repeated using a combination of H_2SO_4 (0.1 mol L^{-1}) and $K_2S_2O_8$ (9.8 g L^{-1}). As a conversion value of 95% was obtained, further studies were carried out using this mixture.

Firstly, the concentration of $K_2S_2O_8$ was fixed at 24.5 g L^{-1} and the concentration of H_2SO_4 was varied from 0.05 to 0.6 mol L^{-1}; the influence of the acid concentration on the conversion percentage of four organic compounds is depicted in Fig. 3a. Better results for all phosphorus compounds corresponded to the 0.4 mol L^{-1} solution. Therefore, this concentration was used to study the influence of the $K_2S_2O_8$ concentration between 6.12 and 30.6 g L^{-1} (Fig. 3b). From 18.4 to 30.6 g L^{-1}, the conversion was not increased for the compounds tested and a value of 24.5 g L^{-1} was chosen for further experiments. During these studies, it was necessary to add a glass spiral

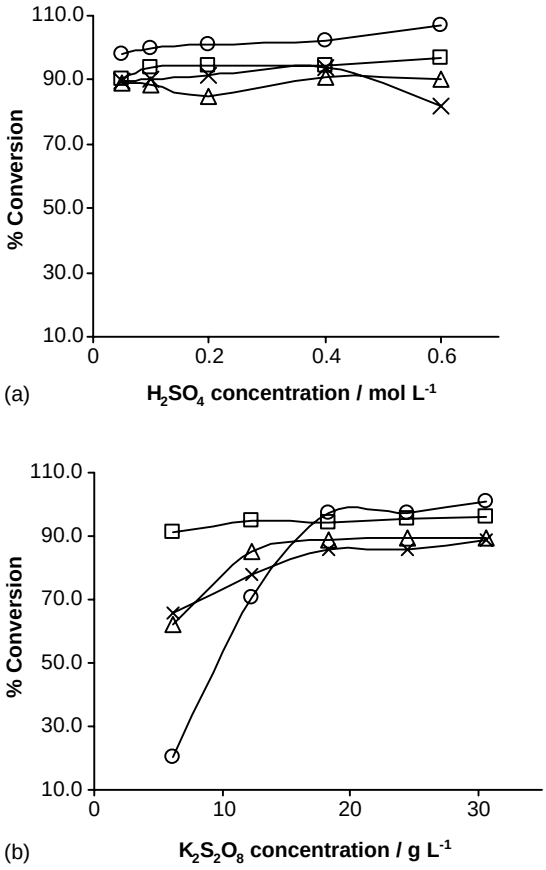

Fig. 3. Variation of percentage of conversion obtained for different concentrations of H_2SO_4 (a) and $K_2S_2O_8$ (b) in the digestion solutions. (□) phenylphosphate; (○) trimethylphosphate; (△) D-glucose 6-phosphate; and (×) phytic acid.

Table 2
Results obtained from the study of the digestion time and microwave power

Power (W)	Digestion time (s)			
	10	20	30	40
465	12 ± 1	12 ± 1	65 ± 5	85 ± 2
595	12 ± 1	13 ± 1	88 ± 3	92 ± 2
700	74 ± 7	87 ± 2	88 ± 3	93 ± 2

The values correspond to the conversion percentage of the phytic acid ($12\,mg\,P\,L^{-1}$).

to the exit aperture of the digestion vessel, as intense bubble formation occurred upon MW heating.

Using the chosen digestion solution (H_2SO_4 $0.4\,mol\,L^{-1}$ + $K_2S_2O_8$ $24.5\,g\,L^{-1}$), digestion time and the power set on the MW oven were studied using phytic acid as model compound. Digestion times between 10 and 40 s were tested at three different power values (465, 595, and 700 W). The results obtained are given in Table 2. In general, the increase of both digestion time and power led to higher conversion percentage, although very similar at 595 and 700 W for a digestion time higher than 30 s. Better results corresponded to 30 and 40 s at 595 and 700 W. As back-flush occurred when digestion was performed at the maximum power during 40 s and the difference between the results obtained for 30 and 40 s (at 595 W) were not significant, digestion during 30 s at 595 W was chosen.

Finally, other phosphate compounds (sodium diphosphate, sodium triphosphate, and adenosine 5′-triphosphate), including inorganic condensed phosphates, were tested; the results obtained did not exceed 10% of conversion, using the given conditions.

3.4. Application to water samples

The proposed system was applied to the determination of total phosphorus in seven waste water samples. The results were compared with those furnished by the reference method [15]. They are presented in Table 3.

To evaluate the accuracy of the developed methodology, a statistical treatment of MSFIA results was established by a relation type $C_{MSFIA} = 1.07\ (\pm 0.11)\ C_{RM} - 0.83\ (\pm 0.92)$, $R = 0.996$, where values in parenthesis are 95% confidence limits [16]. No evidence for systematic difference between the two sets of results was found since the estimated slope and intercept do not differ significantly from 1 and 0, respectively.

Table 3
Results obtained by MSFIA methodology (C_{MSFIA}) and by the reference method (C_{RM}) for the determination of total phosphorus in waste water samples

Samples	C_{MSFIA} ($mg\,P\,L^{-1}$)	C_{RM} ($mg\,P\,L^{-1}$)	A.D. ($mg\,P\,L^{-1}$)	R.D. (%)
1	11.3 ± 0.1	11.1 ± 0.1	0.2	1.8
2	9.5 ± 0.2	9.5 ± 0.1	0.0	0.0
3	5.1 ± 0.2	5.3 ± 0.1	−0.2	−3.8
4	7.3 ± 0.3	7.8 ± 0.0	−0.5	−6.4
5	5.2 ± 0.1	5.6 ±0.1	−0.4	−7.1
6	7.5 ± 0.2	7.9 ± 0.1	−0.4	−5.5
7	9.1 ± 0.3	9.4 ± 0.1	−0.3	−3.3

Absolute (A.D.) and relative deviations (R.D.) are also given.

Repeatability was assessed by calculating the relative standard deviation from 15 consecutive determinations (five digestions with three determinations) of four solutions ($12\,mg\,P\,L^{-1}$) of phosphorus compounds. Relative standard deviations were <2.41% for solutions containing phenylphosphate, trimethylphosphate, D-glucose 6-phosphate, and phytic acid.

The detection limit was calculated as the concentration corresponding to the blank signal plus three times the standard deviation of 12 consecutive blank injections (four digestions with three replicate determinations). The value obtained was $0.9\,mg\,P\,L^{-1}$.

The analytical cycle of the present methodology can be divided in three parts: sample preparation (Table 1, steps A–K), colorimetric determination of phosphate (Table 1, steps L and M), and washing of the system (Table 1, steps N–R). Considering that the time required for data transference between the computer and the multi-syringe must also be accounted, it took 136 s for sample preparation, 163 s for each determination, and 300 s for the washing of the system. For sample analysis, the whole procedure took 925 s as the colorimetric determination was repeated three times for each sample. In this case, the sample frequency was about $4\,h^{-1}$, but the determination frequency was $12\,h^{-1}$.

4. Conclusions

In the present work, microwave in-line digestion was implemented in a MSFIA system for the first time. The described methodology combined positive aspects of both FIA and SIA techniques. It was possible to move solutions through two or more channels simultaneously, as occur in FIA. On the other hand, the digestion vessel was operated discontinuously, as solutions were propelled or drawn from it through the same channel after flow reversal. This type of operation avoided the passage of air bubbles into the flow system, without relying on any other type of device.

Total phosphorus determination was carried out successfully in domestic waste water samples, in spite of the fair conversion obtained when inorganic condensed phosphorus compounds were tested. Probably the temperature was not sufficiently high and the digestion time was not long enough. For this reason, determination of total phosphorus in other types of environmental samples should be considered carefully if the conditions described here are applied. Otherwise, modifications in digestion conditions (time, MW power, composition of digestion solution) could be introduced.

Finally, the present method can be considered a contribution towards green analytical chemistry as it reduces not only the amount of reagents but also the energy necessary to carry out the digestion process.

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