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Direct Introduction of Slurry Samples in Multi-syringe Flow Injection Analysis: Determination of Potassium in Plant Samples

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The present work explores the slurry sampling approach for automatic, flow-based plant analysis. For this purpose, pinch valves were introduced into a multi-syringe flow injection analysis manifold to provide the repeatable aspiration of a few microliters of plant suspension before the material was further processed through the flow system. For validation of the proposed approach, the determination of potassium by flame emission spectrometry was implemented. Several parameters were studied: the concentration of plant particles in the sample suspension and the utilization of matrix modifiers. Microwave digestion was also implemented; no significant difference was found when certified reference material was analyzed with or without the in-line digestion step. The system was successfully applied to 13 samples within a concentration range of 2.5 to 100 mg g^{-1}. A determination frequency of 28 h^{-1} was achieved and the precision was better than 4.0% (n = 12).

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Introduction

Potassium is an essential nutrient and a major constituent within all living cells, and is required in large amounts by plants, animals and humans. Humans obtain the majority of their potassium either directly from plants or indirectly through the animal products in their diet. Therefore, it is very important to maintain the appropriate level of plant-available potassium in soil to ensure adequate plant growth.[1]

Thus, plant analysis arises as a logical complement to soil analysis to evaluate the nutrient availability and to issue fertilization recommendations. Nevertheless, these analyses are usually labor-intensive and time consuming. As a consequence, the required real time answer is not provided, especially during the short planting season.[2]

Flow techniques have become consolidated as one of the most efficient and versatile methods in agricultural laboratories.[3] The possibility of in-line sample treatment and the capability to handle solid samples are some of the features that meet the analytical requirements of the agricultural field, decreasing significantly the overall analysis time. The accuracy and repeatability of the assay may also be enhanced, as the "extraction step", involving the transfer of the target analyte to solution and/or solubilization of the plant matrix, is eliminated or performed in-line.

As a robust, easily adaptable and fully computer controlled multi-channel technique, multi-syringe flow injection analysis (MSFIA) has a high potential for the automation of sample pretreatments.[4,5] However, its application to solid samples was only tested once, using a flow-through microcolumn assembly,[6] which contained the solid material. The analyte was, thus, continuously leached and the particulate matter was retained. Another alternative for the direct introduction of solids into flow systems is the introduction of powdered or disperse solids as slurries.[7] This approach has been applied to the direct insertion of plant samples into flow systems by means of injection valves/commutators[8-10] or selection valves.[11,12] The use of pinch valves for the same aim was reported in theoretical studies using model solutions[13] and a nitrogen flow to propel the slurry samples,[14] without application to real samples.

Therefore, the purpose of this work was to explore the slurry sampling approach for automatic analysis of plant materials using a MSFIA manifold equipped with pinch valves. In order to demonstrate the applicability of the proposed approach, the determination of potassium in plants by flame emission spectrometry was implemented.

As the reference procedure[15] comprehends a hot-acid digestion step for extraction of potassium from the plant material, a microwave oven was included in the MSFIA manifold to enable in-line sample digestion. Besides the digestion conditions, other parameters related to the preparation and insertion of slurries into the flow manifold were also addressed.

Experimental

Reagents and solutions

All chemicals were of analytical-reagent grade and deionized

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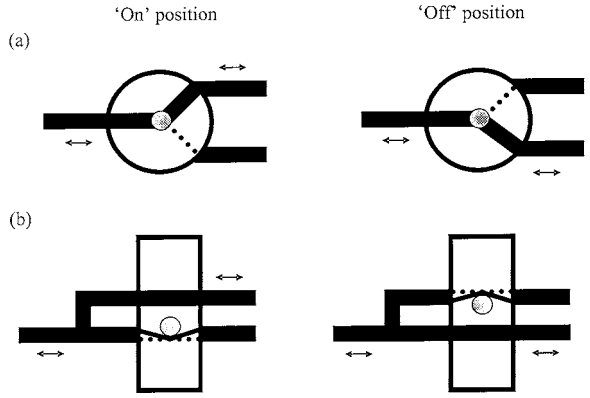

Fig. 1 Schematic representation of a commutation valve (a), and a pinch valve (b). The "on" and "off" positions are shown on the left and on the right side of the figure, respectively, for both solenoid valves.

water was used for the preparation of all the solutions. A stock solution of 25% (w/v) Triton X-100 was obtained by adding 26.8 g of the reagent into 75 mL of tepid water to facilitate dissolution. A potassium stock solution of 1000 mg L^{-1} was prepared by dissolving 0.1907 g of potassium chloride (previously dried at 100°C overnight) in 100 mL of water. Working standard solutions (20.0 – 200 mg L^{-1}) were obtained by suitable dilution of the above stock solution and contained 5% (v/v) Triton X-100. A nitric acid solution (6.0 mol L^{-1}) was also used.

The digestion mixture used in the reference method was prepared by dissolving 7.2 g of salicylic acid in 100 mL of the sulfuric acid-selenium mixture (3.5 g of selenium in 1 L of sulfuric acid 96% (w/w), heated to 300°C for about 3 – 4 h).

Plant materials

Parsley (*Petroselinum crispum*), turnip greens (*Brassica rapa*), watercress (*Nasturtium officinale*), lettuce (*Lactuca sativa*), celery (*Apium graveolens*), and bay leaves (*Laurus nobilis*) were purchased from local food stores. Oak leaves (*Quercus robur*), olive leaves (*Olea europaea*), lemon leaves (*Citrus limonum*), collard greens (*Brassica oleracea*), tangelo leaves (*Citrus paradisi* × *Citrus reticulata*), passion-fruit leaves (*Passiflora edulis*), and pine needles (*Pinus pinaster*) were collected from three sites in the north of Portugal (Paredes de Coura, Ermesinde and Porto). All plant materials were washed with tap water, rinsed with deionized water, dried at 70°C during 24 h, finely powdered and passed through 0.5 and 0.2 mm sieves (for reference and MSFIA methods, respectively). The drying procedure was repeated just before weighing each sample for analysis.

Studies with the microwave digestion were carried out with standard reference material SRM 1570a (spinach leaves) from the National Institute of Standards & Technology and certified reference material CRM 129 (hay powder) from the Community Bureau of Reference-BCR. Both samples were purchased from LGC Promochem (Barcelona, Spain).

Apparatus

Solutions were propelled through the flow network by means of a multi-syringe burette (Crison Instruments, Allela, Spain). This device is a multiple-channel piston pump, containing up to four syringes, driven by a single motor, controlled by computer software through a serial port. In the in-line microwave digestion system, two syringes of 10 mL were placed in positions 1 and 4, and one syringe of 5 mL was placed in position 2, while position 3 was not occupied. In the system

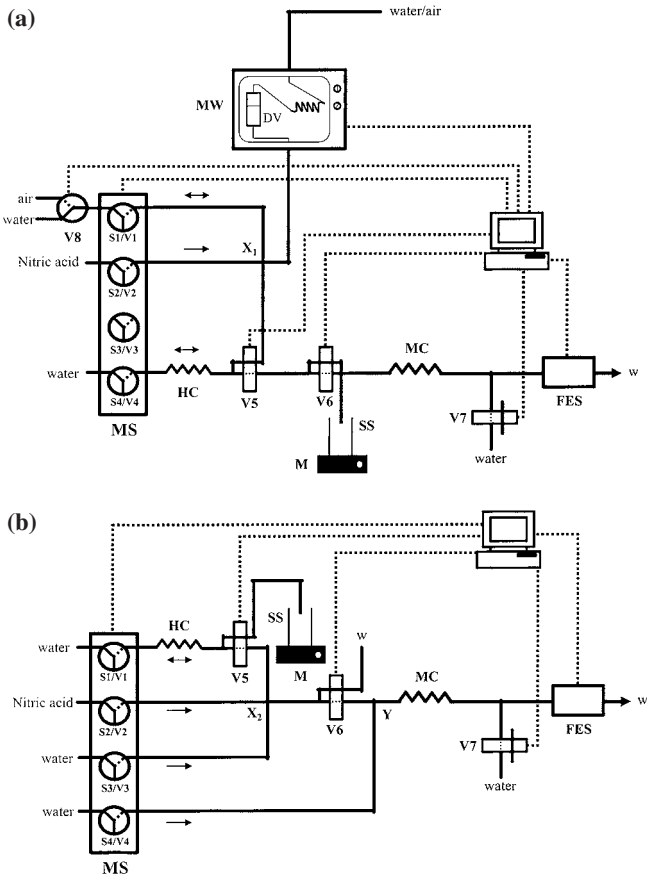

Fig. 2 MSFIA system with (a) or without (b) in-line microwave digestion for the flame emission determination of potassium in plant suspensions. MS, multi-syringe; S*i*, syringe; V1 – V4, V8, commutation valves; V5 – V7, pinch valves; SS, slurry sample; M, magnetic stirrer; HC, holding coil; MC, mixing coil; w, waste; MW, microwave oven; DV, digestion vessel; FES, flame emission spectrometer.

without in-line microwave digestion, two syringes of 5 mL each were placed in positions 1 and 2. The remaining positions were filled by syringes of 10 mL. Two types of solenoid valves (NResearch, Caldwell, NJ) were used: the head of each syringe was connected to a commutation valve (Fig. 1a) while the manifold was assembled using three pinch valves (Fig. 1b; ref. 225P091-21). For all solenoid 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 (represented with a solid and dotted line, respectively, in Figs. 1 and 2), except for V7 (the "off" line was assigned to the water flask).

The solenoid pinch valves contained two silicone tubes (0.8 mm i.d.); one of them was opened while the other was closed. By actuation of the solenoid, this condition was changed, and the first tube was closed while the other was opened. Therefore, for each valve both silicone tubes were joined by glass confluences, enabling their utilization as a commutation valve. In preliminary experiments, commutation valves (NResearch) with an internal volume of 27 μL (ref. 161T031) or 57 μL (ref. HP225T031) were also applied (Fig. 1a).

A personal computer (Digital FR-746WW-A9), running lab-made software written in QuickBasic 4.5 (Microsoft), controlled the multi-syringe operation (number of steps, direction of piston displacement and position of all solenoid valves) and the

Table 1 Protocol sequence for the potassium determination with in-line microwave digestion

Step	Volume/ mL	Flow rate[a]/ mL min^{-1}	Operation	Position of solenoid valve[b]							Description
				V1	V2	V4	V5	V6	V7	V8	
1	0.300	0.6	Pick up	N	N	F	F	N	F	F	Slurry is aspirated.
2	0.250	0.6	Pick up	N	N	F	F	N	F	F	Air is aspirated to place the slurry inside HC.
3	0.800	4.0	Dispense	N	F	F	N	N	F	F	Slurry is merged with nitric acid and send to the MW.
4	0.700	6.0	Dispense	F	N	N	F	N	F	F	Air is pumped to push the mixture inside the DV.
5	1.000	2.4/1.2[c]	Dispense	N	N	F	F	N	F	F	MW is switched on and sampling tube is washed.
6	0.900	3.0	Pick up	F	N	N	F	F	F	F	Air is aspirated from the tubing between DV and X1.
7	0.500	3.0	Pick up	N	N	F	N	F	F	F	Digested slurry is aspirated up to the HC.
8	1.400	5.0	Dispense	N	N	F	F	N	F	F	HC is washed through the sampling tube.
9	1.400	5.0	Dispense	N	N	F	F	F	N	N	The baseline is set.
10	2.500	8.0	Pick up	N	N	N	F	F	F	N	The syringes are filled.
11	0.060[d]	3.0	Pick up	N	N	F	N	F	F	F	Digested slurry is aspirated into the HC.
12	2.800[d]	5.0	Dispense	N	N	F	F	F	N	N	Detection and data acquisition.
13	2.740[d]	6.0	Pick up	N	N	N	F	F	F	N	The syringes are filled.
14	1.350	8.0	Pick up	N	N	N	F	F	F	N	The syringes are filled.
15	9.500	5.0	Dispense	F	N	F	N	F	F	F	Digestion vessel is washed.
16	9.000	8.0	Pick up	F	N	N	F	F	F	F	The syringes are filled.

a. The indicated values for flow rate and volume refer to a 10 mL syringe. b. N and F represent "on" and "off" position, respectively. c. MW activation time was controlled by the flow rate: 2.4 and 1.2 mL min^{-1} corresponded to 25 and 50 s of activation, respectively. d. These steps were repeated three times. Note: Solenoid valve V3 was always switched off.

microwave oven activation. Data acquisition was performed through a PCL-711B interface card at 4 Hz, using the software developed for controlling the flow system. The data obtained was analyzed using Microsoft Excel (Windows XP Professional, 2002). Potassium measurements, both in MSFIA and reference methods, were carried out using a Model 410 flame photometer (Corning, Halstead, England).

For preliminary studies, a domestic Becken MWB 1000 microwave oven was used at maximum power (700 W). Inside the microwave oven was placed a lab-made PTFE digestion vessel, described in detail elsewhere.[16]

MSFIA manifold and procedure

All connections were made of PTFE tubing (Omnifit, Boonton, NJ) with Gilson end-fittings and connectors. The internal diameter of tubing was 0.8 mm, except for the sampling tube (1.0 mm i.d.). The holding coil and the mixing coil were 400 and 100 cm long, respectively, and the sampling tube was 9 cm long.

Preliminary studies were carried out with a microwave oven placed in the MSFIA manifold (Fig. 2a) to enable in-line sample digestion. The applied analytical cycle is explained in Table 1; it involved four parts: slurry sampling, in-line microwave digestion, flame emission determination and washing of the system. Firstly, 0.300 mL of homogeneous plant suspension was slowly aspirated toward the holding coil (HC) followed by air aspiration (steps 1 and 2) in order to place the sample suspension inside the HC. After flow reversal, 0.800 mL of suspension and 0.400 mL of nitric acid were merged in confluence X1 and directed to the digestion vessel (step 3). Then, this mixture was pushed inside the vessel by air propelled from syringe S1 (step 4). After that, the microwave oven was activated at 700 W while the sampling tubing was washed (step 5). During digestion, a beaker containing 200 mL of water was placed inside the microwave oven, to absorb the excess of the radiation. Afterward, the digested sample was aspirated up to the beginning of the HC, after elimination through syringe S1 of the air placed between the digestion vessel and X1 (steps 6 and 7). After the HC was washed with water, the baseline was set and the syringes were filled (steps 8 to 10). The flame emission determination started with aspiration of 0.060 mL of digested sample to the HC (step 11). After flow reversal, the sample was dispersed along the mixing coil (MC) towards the detector for data acquisition (step 12). After the syringes were filled to their initial position, these two steps were repeated twice more, in order to obtain three replicates (step 13). The subsequent steps corresponded to the washing of the system. After the syringes were filled up to 50% of their capacity (V8 switched on to fill S1 with water), the digestion vessel was washed with water provided by syringes S1 and S4 (steps 14 and 15). While the syringes were filled up to 90% of their capacity, the tubes involved in the digestion process were emptied (step 16), so that another analytical cycle could begin.

While these steps occurred, the flame emission spectrometer had to be constantly supplied with water. Therefore, a pinch valve was employed (only one silicone tube was used) together with a "T" piece interface. Thus, when the tube was closed, solutions were propelled from the syringes (5 mL min^{-1}) to perform the flame emission determination. Otherwise, when the tube was opened, the nebulizer was fed with water, directly aspirated by the FES apparatus (4 mL min^{-1}).

After the MSFIA manifold was redesigned (Fig. 2b), the protocol sequence had to be adjusted (Table 2), considering the elimination of the digestion procedure. The slurry sampling operations were similar to those described above. Hence, 0.300 mL of homogeneous plant suspension was aspirated toward the HC, followed by an air plug (step 2). Then, the flow was reversed and the slurry sample was propelled up to confluence X2 (step 3). After the tube between X2 and V6 was washed toward waste, the baseline was established (steps 4 and 5). The flame emission determination of potassium was achieved by dispensing equal volumes (0.025 mL) of slurry and nitric acid at the same time (step 6). This mixture was afterwards merged with water in confluence Y to attain a suitable dilution before reaching the detector (step 7). These two steps were performed three times. To prepare the system for another analytical cycle, the syringes were filled to 50% of their capacity (step 8) and then the system was washed: HC, sampling tube and tubes

Table 2 Protocol sequence for the flame emission determination of potassium in plant samples

Step	Volume/ mL	Flow rate[a]/ mL min^{-1}	Operation	Position of solenoid valve[b]							Description
				V1	V2	V3	V4	V5	V6	V7	
1	0.600	1.2	Pick up	F	N	N	N	N	F	F	Slurry is aspirated.
2	0.400	1.2	Pick up	F	N	N	N	N	F	F	Air is aspirated to place the slurry inside HC.
3	0.320	3.0	Dispense	F	N	N	N	F	N	F	Slurry is sent up to the X2.
4	1.000	5.0	Dispense	N	N	F	N	N	N	F	Tubing between X2 and V6 is washed.
5	0.700	2.5	Dispense	N	N	F	F	N	F	N	The baseline is set.
6	0.050[c]	2.5	Dispense	F	F	F	N	F	F	F	Slurry and nitric acid are injected.
7	1.250[c]	2.5	Dispense	N	N	F	F	N	F	N	Detection and data acquisition.
8	1.420	6.0	Pick up	N	N	N	N	F	F	F	The syringes are filled.
9	3.000	5.0	Dispense	F	N	F	N	N	N	F	HC is washed.
10	2.000	5.0	Dispense	F	N	F	N	F	N	F	Tubing between V5 and V6 are washed.
11	8.500	6.0	Pick up	N	N	N	N	F	F	F	The syringes are filled.

a. The indicated values for flow rate and volume refer to a 10 mL syringe. b. N and F represent "on" and "off" position, respectively. c. These steps were repeated three times.

between V5 and V6 (steps 9 and 10). Finally, the syringes were refilled to their initial position (85% of their capacity).

Slurry preparation

Plant materials (grinded to a particle size <200 μm and dried at 70°C) were directly introduced into the MSFIA system without pretreatment. Hence, about 0.050, 0.100 or 0.200 g of powder was accurately weighed into a 25.00 mL volumetric flask and 5.0 mL of 25% (w/v) Triton X-100 was added before completing the volume with water. During the sampling step, the above preparation was placed on a magnetic stirrer to guarantee the homogeneity of the suspension.[12]

By using different slurry concentrations, we could achieve three potassium concentration ranges: 10 to 100 mg g^{-1} (2.0 mg mL^{-1}), 5.0 to 50 mg g^{-1} (4.0 mg mL^{-1}) and 2.5 to 25 mg g^{-1} (8.0 mg mL^{-1}). Hence, according to the predicted potassium content for a plant sample, the proper slurry concentration was chosen. The reference materials were prepared likewise and suspensions containing 4.0 mg of reference sample per mL were applied.

Sample treatment according to the reference method

Some dried plant material sample (0.3 g) was introduced in a digestion tube with 2.5 mL of digestion mixture. After the material was allowed to stand for at least 2 h, the digestion tube was placed in a heating block at 100°C for about 2 h (minimum). Then, at room temperature, three 1 mL aliquots of hydrogen peroxide were added. The digestion tube was placed, once again, in the preheated block and heated at 330°C for another 2 h. After room temperature was reached, 48.3 mL of water was added and the digest was allowed to stand overnight before analysis. Digests were diluted (10 to 50 times) in order to fit the linear concentration range of the flame emission photometer.[15]

Results and Discussion

Direct introduction of slurry samples in MSFIA

As the main purpose of this work was to introduce slurries directly into the manifold, different types of solenoid valves were tested with slurries containing 4 mg of plant material per mL and a particle size lower than 500 μm. Initially, commutation valves with an internal volume of 27 or 57 μL were incorporated in the manifold, but clogging occurred because solids were trapped in the channels and in the cavity that exist inside the valves. Then, these valves were replaced by pinch valves. In this case, no retention of solids was observed because the sample was aspirated through a cylindrical channel without significant changes in the flow direction.

Because it is crucial to guarantee the slurry stabilization and homogeneity in order to achieve a representative sampling process, the slurry composition was evaluated. Slurries containing 2.0, 4.0 and 8.0 mg of plant material per mL (particle size <500 μm) were prepared in water, in Triton X-100 (0.5, 1, 2 and 5%) and in glycerol (2 and 5%). Each suspension was aspirated into the holding coil (300 μL, flow rate of 0.6 mL min^{-1}), followed by air plug aspiration. For the lowest concentration tested (2.0 mg of plant material per mL), clogging was observed only for the water-based suspensions. Retention of particles in the tubing adjacent to the pinch valve was also observed for slurries containing 4 mg mL^{-1} prepared in water and in glycerol. For the same particle concentration, the suspensions stabilized with Triton X-100 (0.5, 1, 2 and 5%) were successfully aspirated. For slurries containing 8 mg mL^{-1}, only those prepared in 5% Triton X-100 were aspirated without clogging. Hence, 5% Triton X-100 was chosen as modifier for slurries stabilization, since it enabled direct slurry sampling for all particle concentrations tested. This study was developed using bay leaves. However, when other samples were introduced, clogging occurred occasionally. Hence, all samples were re-grinded to a particle size <200 μm and this problem was no longer observed.

After slurry aspiration, the sampling tube was removed from the sample suspension, followed by air aspiration in order to place the slurry inside the HC (step 2, Table 1 or 2). This option was taken to minimize the volume of sample suspension introduced into the flow system and to avoid the deposition of solid particles in the sampling tubing.

Implementation of in-line microwave digestion

The MSFIA manifold was initially designed to enable direct introduction and in-line digestion of plant solid samples, followed by flame emission determination of potassium (Fig. 2a). Hence, slurries were merged with digestion solution after confluence X1, before achieving the digestion vessel placed inside the microwave oven. After a fixed time interval, the digested sample was retrieved and sent to the flame photometer.

To evaluate the digestion efficiency, we used two certified samples. The digestion time was studied (25 and 50 s) at 700 W, while 6 mol L^{-1} nitric acid was used as digestion solution (Table 3). The results obtained were similar: with 25 and 50 s

Table 3 Results obtained for the reference materials using the MSFIA system with in-line microwave digestion (0, 25 and 50 s correspond to the microwave activation times studied)

Reference material	Activation of microwave/mg g^{-1}			Reference value/mg g^{-1}
	0 s	25 s	50 s	
SRM 1570a	29.4 ± 0.5	28.9 ± 0.1	29.6 ± 0.3	29.03 ± 0.52
(Spinach leaves)[a]	30.0 ± 0.7	29.7 ± 0.5	29.0 ± 0.7	
CRM 129	33.0 ± 0.7	32.9 ± 0.2	32.5 ± 0.9	33.8 ± 0.8
(Hay powder)[a]	32.5 ± 0.1	32.7 ± 0.6	32.8 ± 0.2	

a. Two samplings with three replicates each.

of microwave action, recoveries higher than 99.6 and 100% were achieved for spinach leaves, while recoveries higher than 96.7 and 96.2% were attained for hay powder. Considering these results, we performed the same experiment with the microwave switched off. The recovery percentages obtained were about 101 and 96.0% for spinach and hay powder, respectively. One-way ANOVA analysis was thus applied to assess the existence of significant differences among the three conditions studied (each comprising two sampling steps with three replicate determinations). The calculated F values for spinach and hay powder samples were 1.01 and 0.08, values lower than the critical F value ($F_{2,15}$ = 3.68) for a level of confidence of 95%.[17] This indicates that the variance among the three digestion conditions is not significantly different from the variance obtained within the three consecutive measurements performed in each sampling. Hence, it can be acknowledged that the microwave action was not necessary. Considering that potassium exists in plants mainly in its inorganic ion form (K^+), we concluded that its solubilisation may not require such drastic conditions as those necessary for recuperation of elements that are part of organic molecules. As a consequence of these results, the MSFIA manifold was redesigned and the microwave digestion step was excluded.

MSFIA system for the determination of potassium in slurry plant samples

The MSFIA manifold was modified in order to allow introduction of slurry samples followed by flame emission determination of potassium (Fig. 2b). Despite the exclusion of the microwave digestion step, the dilution factor had to be maintained considering the concentration range attained by the flame emission detector. Hence, with the same slurry sampling strategy, the injection volume was reduced to 25 μL and two additional dilution channels were inserted. Slurries were merged with acid solution and water by means of confluence X2 and this mixture was further merged with another dilution channel in confluence Y.

The proposed system was applied to thirteen plant samples within a wide concentration range. The results were compared with those furnished by the reference method[15] and are presented in Table 4. In order to assess the accuracy of the developed methodology, a linear relationship ($C_{MSFIA} = S \times C_{RM} + C_0$) was established. Plant samples were divided in two groups: one including vegetables (higher content of K) and the other including non-edible plant leaves (lower content of K). Hence, C_{MSFIA} = 0.994(±0.097) × C_{RM} − 0.6(±4.8), R = 0.997 was obtained for the vegetable group (n = 6) and C_{MSFIA} = 1.033(±0.073) × C_{RM} + 0.02(±0.62), R = 0.998 was obtained for the other group (n = 7), where the values inside parentheses are 95% confidence limits.[17] Considering these values, we concluded that the estimated slope and intercept do not differ significantly from 1 and 0, respectively, for both groups. Therefore, there is no evidence for systematic differences between the sets of results obtained by the proposed methodology and those obtained by the reference method. A paired t-test was also applied. The calculated t (0.992) was lower than the critical t value (2.179, p = 0.05, $d.f.$ = 12), which also indicates the absence of systematic differences between the results of the two methods.[17]

Table 4 Results obtained by the proposed MSFIA methodology (C_{MSFIA}) and by the reference method (C_{RM}) for the flame emission determination of potassium in plant samples

Plant sample	Slurry concentration/ mg mL^{-1}	C_{MSFIA}/ mg g^{-1}	C_{RM}/ mg g^{-1}	RD, %
Parsley	2.0	54.7 ± 2.2	56.4 ± 0.7	–3.0
Watercress		52.6 ± 0.4	52.9 ± 0.4	–0.6
Lettuce		66.7 ± 1.0	67.1 ± 0.9	–0.6
Celery		36.3 ± 1.2	35.8 ± 0.3	1.4
Passion-fruit leaves	4.0	14.3 ± 0.5	14.1 ± 0.1	1.4
Collard greens		27.9 ± 1.2	28.8 ± 0.2	–3.1
Turnip greens		41.7 ± 1.1	43.9 ± 0.3	–5.0
Bay leaves		8.70 ± 0.35	8.59 ± 0.17	1.3
Tangelo leaves	8.0	4.69 ± 0.28	4.33 ± 0.04	8.3
Lemon leaves		3.43 ± 0.21	3.34 ± 0.03	2.7
Pine needles		4.91 ± 0.26	4.73 ± 0.07	3.8
Oak leaves		5.22 ± 0.18	5.21 ± 0.07	0.2
Olive leaves		12.9 ± 0.4	12.0 ± 0.2	7.5

The slurry concentration applied to each sample and the relative deviations (RD) are also given.

The repeatability was assessed by calculating the relative standard deviation from 12 consecutive determinations (four samplings with three replicates each) for three plant samples containing different concentrations of potassium (5.00, 14.8 and 54.7 mg g^{-1}). The corresponding relative standard deviation values were lower than 2.5, 3.9 and 4.0%, respectively.

The detection limit was calculated as the concentration corresponding to the blank signal plus three times the standard deviation of twelve consecutive blank injections. The values obtained, for slurries containing 2.0, 4.0 or 8.0 mg of plant material per mL, were 1.9, 0.96 and 0.48 mg g^{-1}, respectively.

The analytical cycle of the present methodology can be divided in three parts: slurry sampling (Table 2, steps 1 to 5), flame emission determination of potassium (Table 2, steps 6 and 7) and washing of the system (Table 2, steps 8 to 11). Considering that the time required for data transference between the computer and the multi-syringe must also be accounted, it took 100 s for slurry sampling, 110 s for potassium determination (in triplicate) and 174 s for the washing of the system. Hence, the sample frequency was about 9.4 h^{-1}, but the determination frequency was about 28 h^{-1}.

Conclusion

The developed MSFIA system offers a sound alternative for determination of K in plants when compared to the usual reference method that comprises a digestion procedure that takes several hours. The flow strategy proposed here allowed the direct introduction of the solid sample in the flame emission photometer, which is not feasible in the batch mode because of fouling and clogging that occurs along the sample tubing and

burner. To avoid these problems, the manifold enabled the introduction of a low volume of suspension (25 μL) with subsequent continuous washing of all tubing and detector by carrier. Furthermore, the utilization of pinch valves was suitable for handling slurry samples in a repeatable fashion; that detail can also be extended to the determination of other metals using flame or plasma-based detectors.

In this particular analytical task, the microwave digestion was dispensable as the results obtained without it for 15 samples (including certified reference material) were statistically comparable to those attained using the batch method, comprising a hot-acid digestion. Nevertheless, the proposed configuration succeeded in handling both slurry sampling and in-line microwave digestion, which forecasts its application to the determination of other analytes (iron, for instance) in plant samples. Finally, the system was successfully applied to different plant samples within a wide potassium concentration range (2.5 to 100 mg g^{-1}) with a significant improvement of the overall analysis time and sample handling.

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