Article

On-line Digestion in a Focused Microwave-Assisted Oven for Elements Determination in Orange Juice by Inductively Coupled Plasma Optical Emission Spectrometry

Sabrina P. Fili, Elisabeth Oliveira and Pedro V. Oliveira*

Instituto de Química, Universidade de São Paulo, 26077, 05513-970 São Paulo - SP, Brasil

Um sistema de fluxo acoplado a um forno de microondas focalizadas foi utilizado para digestão em linha de amostras de suco de laranja para a determinação de Ca, Cu, Fe, K, Mg, Mn, Na, P e Zn por espectrometria de emissão ótica com plasma indutivamente acoplado. Uma bobina de reação de PTFE (4,0 m de comprimento e 1,6 mm de diâmetro interno) foi posicionada no interior da cavidade de vidro do forno de microondas focalizadas. Alíquotas de 500 μL de amostra e de 1000 μL de reagente (80% v/v HNO_3) foram misturadas em uma confluência e conduzidas para a bobina de reação utilizando ar como carregador. O desvio padrão relativo para cinco determinações da mesma amostra usando o método proposto foi inferior a 5,0%. Boas recuperações variando de 91 a 111% foram obtidas para adições de quantidades conhecidas dos elementos de interesse. Os resultados obtidos, utilizando o sistema de digestão proposto, foram concordantes a um nível de confiança de 95% com aqueles obtidos por digestão total. Com este método de digestão foi possível processar 12 amostras h^{-1}, minimizando contaminações, consumo de amostra e reagentes e gerando pequena quantidade de resíduos.

A flow injection system coupled to focused microwave-assisted oven was used for on-line orange juice sample digestion for determination of Ca, Cu, Fe, K, Mg, Mn, Na, P, and Zn by inductively coupled plasma optical emission spectrometry. The reactor coil was a PTFE tube (4.0 m long and 1.6 mm i.d.) positioned into the commercial glass tube of the focused microwave oven. Aliquots of 500 μL of sample and 1000 μL of reagent (80% v/v HNO_3) were mixed in a confluence and carried out to the reactor coil by air carrier. The relative standard deviation for five replicates of sample was lower than 5.0%. Good recoveries varying from 91 to 111% were obtained for added concentrations of the interest elements. The results obtained using the proposed digestion system are in agreement with those obtained for total digestion at the 95% confidence level. With this on-line digestion system was possible to carry out 12 samples h^{-1}, minimizing contamination, saving consumption of samples and reagent and low residue generation.

Keywords: on-line digestion, orange juice, focused microwave oven, atomic emission

Introduction

Major and trace elements levels in orange juice have been a subject of considerable interest due to the relationship between some elements and plant, animal and human nutrition. Additionally, some elements and organic constituents, mainly amino acids, can be used to monitor quality, authenticity and country of origin.[1,2] Chemical characterization of the orange juice may be used to establish guidelines required for quality control monitoring. Adulteration can range from a simple addition of sugar solution to more sophisticated methods, as addition of pulp wash or peel extract to concentrate. Trace metal data are potentially more useful than the major elements for identifying the history of juice and detecting adulteration.[1]

Several spectrometry techniques have been used for macro and trace elements determination in orange juice: atomic absorption spectrometry with flame (FAAS),[3-7] hydride (HGAAS)[8,9] or electrothermal atomization (ETAAS),[10,11] inductively coupled argon plasma optical emission spectrometry (ICP-OES),[1,5,12-17] direct current argon plasma optical emission spectroscopy (DCP-OES),[5] and inductively coupled plasma mass spectrometry (ICP-MS).[1,17]

FAAS methods are restricted to major elements determination in orange juice due to the poor sensitivity. For trace elements, the most recommended techniques are

---

ETAAS, ICP-OES and ICP-MS. Whereas simultaneous ICP-OES or ICP-MS provide rapid multielement analysis which are highly desirable for adulteration investigations, a comparative study of the spectroscopic techniques for elements determination in orange, observing differences between methods with respect to convenience, analytical frequency, precision, detection limits and calibration procedures showed general agreement between final results for all methods.[5] Frequently, the above techniques require introduction of liquid solution for elemental analysis. For this reason, a great number of samples are dissolved or digested in chemical laboratories, making this one of the most common operations within the total analytical procedure.[18]

The usual methods applicable for orange juice sample preparation involve the organic matter destruction. Dry ashing in a muffle furnace,[3,5,7,8,12,13] wet digestion procedure using a hot plate,[4,10,14] or microwave-assisted oven[9,12,13,15-17] have been used as orange juice sample preparation for elemental analysis. For some elements determination, such as Al, a simple filtration has been proposed.[11]

In the last two decades sample preparation has been putting in evidence in many analytical methods published in the literature.[19] Among these, alternative procedures by using flow systems coupled to microwave ovens are one of the most proposed for sample preparation.[20-30] These systems save time, sample requirement and reagent consumption, accelerate the reaction through rapid heating, making it possible to generate reaction products quickly and in lager quantities.[20] Besides of these favorable characteristics, fume production during wet digestion, contamination and losses of volatile elements can be overcome or minimized when flow digestion systems coupled to the microwave oven are used. In a general way, the system in flow is incorporated to a microwave oven, and the digested sample is collected in flasks opened for subsequent analysis by some appropriate analytical technique or driven directly to the detector coupled in line with the microwave oven. Microwave ovens with big cavity, e.g., domestic or commercial are well suitable to couple on-line flow systems for sample digestion. A significant number of papers have described procedures based in this kind of configuration.[20-23]

In spite of the apparent facilities to couple an on-line flow systems, focused microwave-assisted ovens have not awoke to the interest for this arrangement. For this reason, an on-line flow system coupled to focused microwave-assisted oven is proposed for orange juice sample preparation for the determination of Ca, Cu, Fe, K, Mg, Mn, Na, P, and Zn by inductively coupled plasma optical emission spectrometry.

Experimental

Apparatus

A sequential inductively coupled plasma optical spectrometer Spectro Flame (Spectro Analytical Instruments GMBH, Kleve, Germany) equipped with quartz spray chamber torch and concentric nebulizer (Meinhard, TR-20-C1) was used. The instrumental and operational parameters used in this work are described in Table 1. All measurement was based on peak height emission intensity by OS/2 WARP 4 Operating System, with at least three replicates.

Table 1. Instrumental parameters for ICP-OES

Parameter	
RF generator	27 MHz
Operating Power	1200 W
Cooling gas flow-rate	12 L min^{-1}
Auxiliary gas flow-rate	1.2 L min^{-1}
Nebulizer pressure	3.0 bar (300 kPa)
Sample uptake	1.8 L min^{-1}
Observation height	12 mm
Spectral Wavelengths (nm)	Optic 1: Ca = 317.3; Cu = 324.7; Fe = 259.9; Mg = 279.1; Mn = 293.9; P = 178.3; Zn = 334.5 Optic 2: Na=559.0; K=766.5

Argon 99.96% (v/v) (Air Liquid Brasil S/A, São Paulo, Brasil) was used as auxiliary, plasma and sample introduction gas.

The on-line flow system consisted of an Ismatec Model IPC-8 peristaltic pump (Ismatec, Switzerland) furnished with Tygon® pumping and PTFE conducing tubes (0.8 and 1.6 mm i.d.), a three-piece injector commutator with built-in T-shaped connectors (Figure 1, A), a focused microwave-assisted oven (Spex, Merceville, NJ, USA) equipped with a magnetron of 2450 MHz with nominal maximum power of 300 W, and reactor coil adapted in a cooler system (Figure 1, B). The PTFE reactor coil (4.0 m long and 1.6 mm i.d.) (Figure 1,d) was introduced into the microwave oven glass cavity (Figure 1, c). The reactor coil extremities pass inside of a laboratory-made cooler system mounted in PVC tube (15 mm i.d. with 12 cm long) (Figure 1, e). The PVC extremities were closed with rubber stoppers (Figure 1, f), in each one were made two orifices to allow the through passage of the PTFE tube. The PTFE tubes inside the cooler system were coiled (Figure 1, g) to enhance the contact of these tubes with the cool water flowing into the cooler system. During the sample preparation, cool water flows throughout inside the cooler system (in) and (out).
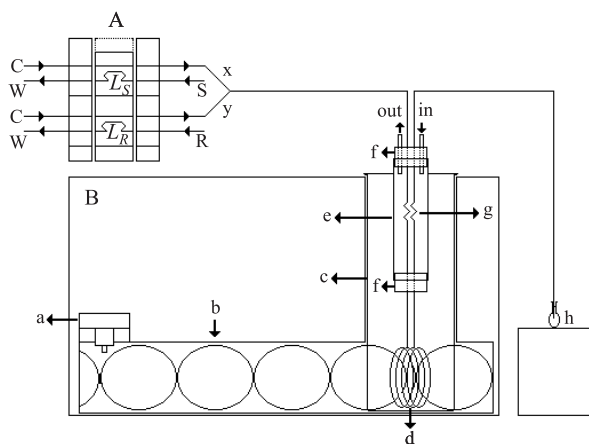
Figure 1. (A): Injector-commutator diagram; S: sample; R: reagent; C: carrier (3.0 ml min⁻¹); W: waste; L_S: sample loop; L_R: reagent loop. (B): On-line focused microwave-assisted sample digestion diagram; a: magnetron; b: waveguide; c: glass cavity; d: PTFE reactor coil; e: PVC cooler system; f: rubber stopper; g: PTFE coils (5cm); and h: volumetric flask (10 mL).

Reagents, reference solutions and samples

All solutions were prepared using high purity de-ionized water (resistivity 18.2 MΩ cm) obtained from a Milli-Q® water purification system (Millipore, Bedford, USA).

High purity reagents or analytical reagent-grade (Merck, Rio de Janeiro, Brasil) were used in all experiments. Hydrogen peroxide and nitric acid were used as reagent for sample preparation. It was purified by distillation in quartz sub-boiling still (Marconi Equipamentos de Laboratório, Piracicaba, Brasil).

Stock reference solutions of 1000 mg L⁻¹ of Ca, Cu, Fe, K, Mg, Mn, Na, P, and Zn were prepared by dissolving Tritisol standard solution (Merck, Darmstadt, Germany), according the instructions of the manufacturer.

The multielement analytical reference solutions containing up to 2 mg L⁻¹ of Cu, Mn and Zn, 20 mg L⁻¹ of Na, 40 mg L⁻¹ of Fe, 200 mg L⁻¹ of Ca, Mg and P, and 400 mg L⁻¹ of K in 1.0% v/v of HNO_3 were prepared by successive dilution of the stock reference solutions. These solutions were used for spectrometer calibration and for addition recovery texts.

Eight commercial orange juices purchased in supermarket were analyzed. All of them were integral juice without additives or water; seven were packing in Tetra Rex (Tetra Pak) case with screw cap and one was packing in plastic (Plaspac) case.

Procedure

All glassware and high-density polypropylene bottles

(Nalge Company, Rochester, USA) were cleaned with detergent solution, soaking in 10% (v/v) HNO_3 during 24 h, rinsed with Milli-Q® water, and stored into a closed polypropylene container. Analytical reference solutions were prepared in a Class-100 laminar flow hood (Veco, Campinas, SP, Brasil).

In the specified position (Figure 1, A), the loop sample (L_S) and the loop reagent (L_R), loaded with 500 μL sample and 1000 μL reagent solution, respectively, were inserted into the air carrier streams (Figure 1, C) at 3.0 mL min⁻¹ and driven towards the confluence point. The distance between the injector-commutator and the confluence for the reagent carrier stream was the half of the sample carrier stream to allow the sampling zone formed by reagent + regent/ sample + reagent. The sampling zone was then directed towards to the PTFE reactor coil located inside the glass flask of the microwave oven (Figure 1, d). When the sampling zone attained the center of the digestion coil, in this system about 20 s, the peristaltic pump was stopped and the microwave program (Table 2) was started. After this heating program, the peristaltic pump was re-started and high pure Milli-Q® water was introduced via the air carrier tubes in order to clear the residual decomposed sample inside the reactor coil. About 1 mL of water was introduced in both, sample and reagent channel. When water passes through the reactor coil, a new sample and reagent loops are injected. The digested sample zone and the water were collected directly into the volumetric flask (10 mL) (Figure 1, h).

Table 2. Heating program for the focused microwave-assisted

Total Digestion Method [a]	
Water Evaporation (Step 1)	45 W – 15 min
Volume HNO_3	5.0 mL
Sample Digestion (Step 2)	30 W – 5 min
	45 W – 10 min
	60 W – 5 min
Volume H_2O_2	2.0 mL
Sample Digestion (Step 3)	60 W – 10 min
On-line Flow Digestion Method [b]	
Step 1	10 W – 1 min
Step 2	0 W – 1 min
Step 3	10 W – 1 min

[a] Sample volume = 5.0 mL, dilution to 25 mL; [b] Sample Volume 0.5 mL, dilution to 10 mL.

Orange juice samples were also digested by conventional system of the focused microwave-assisted oven. For this purpose, 5.0 g of the orange juice samples were accurately weighed and added with 5 mL of concentrated HNO_3 in the digestion vessel and a heating program was executed. After than, 1 mL of H_2O_2 was added and other

heating program was performed (Table 2). After that the solution was diluted to 25.0 mL with Milli-Q® water and analyzed by ICP-OES

Due to the incomplete digestion in the on-line sample decomposition system, small particles persisted in the solution. To prevent Meinhard nebulizer clogging, before the introduction to the ICP-OES, the solutions were filtered in a circular net of Nylon adapted to a PTFE filtration unit, as described in the literature.[31] After each sampling the filter was rinsed with 0.1% v/v of HNO_3 in counter-flow. The ICP-OES sample uptake was matched with the peristaltic pump at 1.8 mL min^{-1}. All analytical reference solutions and the sample solutions processed by conventional digestion were also introduced by this flow system to avoid the inadequate calibration of the ICP-OES and results misjudgment.

The procedures using total digestion and a simple filtration were applied for four orange juices to verify the necessity of sample pretreatment.

Recovery tests were performed by adding 0.5 mg L^{-1} of Cu, Mn and Zn, 5 mg L^{-1} of Na, 10 mg L^{-1} of Fe, 50 mg L^{-1} of Ca, Mg and P, and 100 mg L^{-1} of K to orange juice before and after on-line and conventional digestion procedure.

Results and Discussion

General considerations

The interest for analytical procedures that avoid the complete digestion of solid or liquid samples has been considerably increased in the last years. It is important to stand out that, for some spectroscopy techniques previously mentioned and considering the sample characteristic, in some cases, laborious pretreatment is unnecessary. In this way, microwave-assisted pretreatment accomplished only

by an extraction of the interest element for the aqueous phase, dispensing the lengthy process of the total digestion, saving time and energy requirements are interesting of the analytical point view.

At the first glance, the on-line focused microwave-assisted sample decomposition proposed in this work does not allow a high energetic condition (pressure and temperature) for total samples digestion. The sample zone expansion going out of the microwave region is the main obstacle to get a more aggressive decomposition conditions. However, a moderate heating condition associated to an adequate reaction medium is sufficient to allow the interest element extraction, as observed for orange juice in the on-line decomposition developed in this work.

The direct introduction of the orange juice in an atomic absorption or emission spectrometer through pneumatic nebulization is unfeasible due to the dissolved solids that could provoke capillary tube blockage. On the other hands, the high solids content and the different particle size presented in orange juice to render impossible the direct sample introduction, even so by using special sample introduction system for ICP-OES. In this case, centrifugation or filtration to remove large particles is the recommended procedure before the analysis. Notwithstanding, this procedure consumes a long time (about 1 h to achieve some milliliters with normal filtration), can introduce contamination, and can prejudice the accuracy of the method, some elements associated to the cellular material should be separated in the solid fraction, producing erroneous results. The determination of Ca, Cu, K, Mg and P in the total digested and in the filtrated orange juices showed that the necessity of pretreatment is imperative. For four orange juices determined, Mg, P, K, Ca, and Cu concentrations found in the filtrated were always lower than those obtained for total digestion (Table 3). Phosphorus

Table 3. Comparison of the elements concentration (mg L^{-1}) in orange juice by using total digestion and filtration

	Mg	P	K	Ca	Cu
Sample A					
Total Digestion	123 ± 2	237 ± 3	1651 ± 22	117 ± 2	0.36 ± 0.01
Filtration	110 ± 1	194 ± 2	1462 ± 3	110 ± 4	0.27 ± 0.01
Sample B					
Total Digestion	114 ± 4	197 ± 6	2154 ± 30	98 ± 2	0.25 ± 0.02
Filtration	107 ± 1	149 ± 1	1991 ± 4	68 ± 13	0.15 ± 0.01
Sample C					
Total Digestion	130 ± 1	202 ± 2	2021 ± 7	95 ± 1	0.28 ± 0.01
Filtration	123 ± 1	163 ± 1	1951 ± 9	80 ± 1	0.23 ± 0.01
Sample D					
Total Digestion	137 ± 1	202 ± 1	1863 ± 2	67 ± 1	0.26 ± 0.01
Filtration	131 ± 1	144 ± 1	1857 ± 12	79 ± 1	0.21 ± 0.01

and Cu showed the worst recovery for filtration in comparison with total digestion, about 80 and 70%, respectively.

On-line focused microwave-assisted system optimization

Despite the apparent facility to adapt an on-line flow system to the focused microwave-assisted oven, it is not too easy. One of the most acute difficulties is to maintain the sample and reagent, inside the reactor coil, in the microwave-assisted region during the heating program. It was observed that the sample zone expansion due to the temperature and gases-formation inside de reactor coil is very intense.

No modification was made to the focused microwave-assisted oven to adapt the on-line flow system. For the proposed on-line flow digestion system different reactors lengths (1.0, 2.0 and 4.0 m) and internal diameters (0.8 and 1.6 mm) were tested. These reactors were made of PTFE and the tubes were coiled and put into the original glass cavity of the microwave oven. PTFE tube was used throughout in this work because other material, such as polypropylene, was deformed during the heating program. In all experiments by using reactor coil of 0.8 mm i.d., the pressure generated inside the system was so intense that the sample zone was extended along of the all PTFE tube extension, even for the reactor length of 4.0 m. For this reason, reactors coil of 1.6 mm i.d. were tested. The expansion during the heating program was minimized with this PTFE dimension tubes, being the minor effect observed for reactor length of 4.0 m. However, the expansion of solution persisted.

The introduction of a cooler system mounted in PVC tube in the reactor coil extremities (Figure 1, e) drastically minimized the expansion of the sample zone inside the PTFE tube. During the on-line digestion procedure, cool water flow through this system all time. Besides the reduction expansion, the cooler system refrigerated the digested solution before the reception in the volumetric flask. The PTFE reactor coil with 4.0 m long and 1.6 mm internal diameter were chose for the next experiments.

The sample zone size inside the reactor coil is dependent to the sample and reagent volumes. For optimizatiom, 250, 500 and 1000 μL sample loops and 500, 1000 and 2000 μL reagent loops were tested. To allow the complete interaction of the sample with the reagent, the reagent loop was bigger than sample loop and, in the flow system, the distance "y" was the half of the distance "x" (Figure 1, A) to allow the complete insertion of the orange juice in the reagent, forming a sample zone with reagent + sample/regent + reagent. The dilution factor and

the sample zone extension were considered to choose the loops size.

The flow rate was not critical in this proposed on-line flow digestion system. The adoption of 3.0 mL min^{-1} allowed the sample zone solution attained the reactor coil in 20 s. Higher peristaltic flow rate is not recommended because the digested solution passing through the PVC cooling system is not refrigerated before the volumetric flask.

On-line orange juice sample decomposition

In order to establish the best conditions for orange juice sample preparation by using the proposed on-line flow digestion system, the optimum sample and reagent loops volume, reagent concentration and composition, the heating program, and the dilution factor used for elements determination by using ICP-OES were studied.

By using the proposed on-line decomposition system (Figure 1) with PTFE reactor coil (4.0 m long and 1.6 mm i.d.) and considering the expansion and dilution factor, the best results were obtained by using 500 μL of orange juice loop sample with 1000 μL of reagent loop. As discussed in the previous section, for the low sample loop tested (250 μL), and considering the dilution to 10 mL, the final concentrations of the micro constituents (Cu, Fe, Mn, and Zn) were lower than the detection limits. On the other hand, for 1000 μL, the sample size volume formed with reagent occupied a big part of the reactor coil, intensifying the expansion inside the PTFE tube.

To verity the influence of the nitric acid concentration on the quantitative elements extraction of the orange juice, 10, 50 and 80% v/v of this reagent were tested. A clear solution was obtained when 80% v/v HNO_3 was used as reagent. When 10 or 50% nitric acid concentration were used it was possible to observe a lot of orange juice particle in the digested solution. The recovery for all elements by using 10 or 50% nitric acid concentration were about 81 ± 6% and 87 ± 5% in comparison with the total digestion procedure (Table 2), respectively. The results obtained with these nitric acid concentrations were similar to those obtained for orange juices filtration. Concentrated nitric acid (67% m/v) was avoided due to the observed corrosion in the injector-commutator metallic parts and the fume evolution in the lab ambient. Specifically for orange juice sample decomposition, the addition of hydrogen peroxide in the reagent did not cause benefices. On the contrary, the gases evolution was improved and, consequently, the sample zone expansion.

The heating program was also a critical parameter. The microwave oven used in this work has only time control,

and the minimal time for applying a specific percentage of the total microwave power (300 W) is 1.0 min. The minor power was always selected (10% - 30W) to avoid over-heating of the solution inside the PTFE reactor coil.

The microwave-assisted heating time in the on-line orange juice decomposition was studied (Figure 2). It is important to comment that a step without microwave application was intercepted between others steps with application of 30 W during 1 min. To get 5 min of microwave-assisted time the heating program (Table 2) had a total time of 10 min. It can be seem (Figure 2) that sodium presented the same result with or without microwave heating, showing that this element can be determined by using a simple orange juice dilution. For Ca, K and Mg, after 2 min of microwave-assisted heating the same results were observed for normalized concentration up to 5 min. For the others elements (Cu, Fe, Mn and Zn), the same behavior were observed, from 2.0 min up to 5.0 min the normalized concentrations were practically the same. For phosphorus only 1.0 min of heating was necessary. Based in this results 2.0 min of microwave-assisted heating time were adopted. However, the continue heating during 2.0 min provoked over-heating
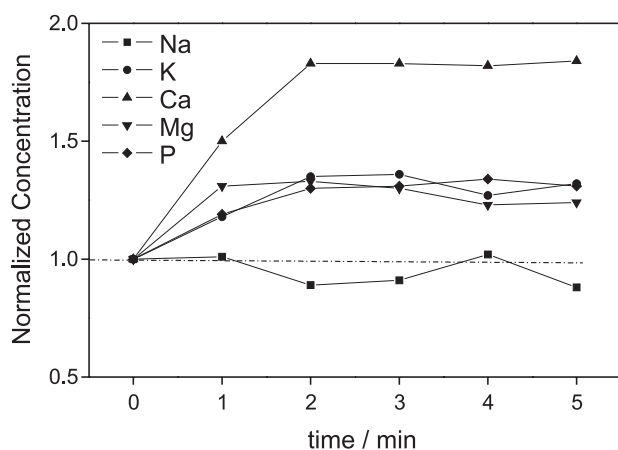
of the solution and an intense expansion of the sample zone. To overcome this effect, a heating program intercalating 1.0 min without microwave application (Table 2) was adopted. This strategy allowed to work up to 5 min of microwave-assisted heating time without over-heat and sample zone expansion.

Elements determination in orange juices

Under optimal on-line flow injection sample digestion and ICP-OES conditions, orange juices samples were analyzed by using the proposed on-line procedure (Table 4). Applying *t*-test, the results by using total and on-line sample pretreatment were found to be similar at the 95% confidence level. Potassium and sodium concentration of sample II are higher than those found for others orange juices. This specific orange juice sample was not a natural juice, in the manufacturer was added soy flour that was informed in the case specifications.

Addition of the interest elements to an orange juice before the on-line flow digestion procedure presented good recoveries (91 to 111%) for all interest elements.

The results obtained for orange juices are in accordance with others presented in the literature, using different sample preparation procedures (Table 5).

Figure 2. Effect of heating program time in the analytical results.

Table 5. Average elemental composition for orange juices from different countries

Element	Concentration (mg L^{-1})		
	This Work [a]	Brazil[b]	Other[b]
Al	0.15 − 0.57	0.06 − 5.67	0.1 − 0.7
Ca	36 − 135	77 − 120	87 − 150
Cu	0.11 − 0.21	0.15 − 0.40	0.1 − 0.4
Fe	0.92 − 3.6	0.80 − 7.49	1.1 − 8.5
K	1981 − 2566	2030 − 3097	1245 − 2465
Mg	102 − 208	107 − 170	82 − 155
Mn	0.38 − 0.56	0.22 − 0.79	0.2 − 0.9
Na	0.46 − 1.30	0.89 − 25.5	2.5 − 43.3
P	176 − 221	155 − 308	104 − 309
Zn	0.26 − 0.35	0.26 − 0.53	0.2 − 0.5

[a] n = 8; [b]by using the on-line flow digestion system.

Table 4. Elements concentrations in orange juices (mg L^{-1})

Element	On-line Sample Digestion Procedure							
	I	II	III	IV	V	VI	VII	VIII
Ca	57 ± 1	135 ± 3	46 ± 2	36 ± 1	64 ± 1	63 ± 2	69 ± 1	49 ± 3
Cu	0.11 ± 0.03	0.12 ± 0.04	0.18 ± 0.02	0.12 ± 0.03	0.21 ± 0.05	0.20 ± 0.02	0.21 ± 0.04	0.17 ± 0.03
Fe	1.4 ± 0.2	3.6 ± 0.6	3.0 ± 0.2	16.4 ± 0.5	2.3 ± 1	0.9 ± 0.5	0.9 ± 0.5	0.7 ± 0.4
K	2214 ± 7	589 ± 10	2399 ± 39	2264 ± 9	2566 ± 19	2288 ± 14	1981 ± 11	2211 ± 7
Mg	208 ± 7	46 ± 2	118 ± 9	102 ± 8	110 ± 4	115 ± 7	104 ± 5	133 ± 3
Mn	0.56 ± 0.12	0.49 ± 0.07	0.44 ± 0.01	0.38 ± 0.16	0.21 ± 0.02	0.44 ± 0.01	0.23 ± 0.05	0.36 ± 0.05
Na	< LD	105 ± 2	0.46 ± 0.02	< LD	< LD	< LD	< LD	< LD
P	180 ± 3	48 ± 3	185 ± 2	176 ± 2	216 ± 2	210 ± 1	198 ± 2	221 ± 3
Zn	< LD	0.99 ± 0.35	0.93 ± 0.23	0.34 ± 0.05	< LD	0.35 ± 0.07	0.28 ± 0.11	0.26 ± 0.04

I to VIII are orange juice samples; LD=Limit of Detection (Na) 0.026 mg L^{-1} and (Zn) 0.050 mg L^{-1}.

Conclusions

The proposed on-line focused microwave-assisted digestion system allowed 12 samples h^{-1} against 1 sample h^{-1} by using the conventional focused microwave-assisted oven for total sample digestion. It is important to emphasize that in this analytical frequency the pretreatment and cooling of the sample solution and ICP-OES determination time are considered. Additionally, in the proposed on-line decomposition system sample and reagent consume are minimized and low residue is generated.

This proposed system is the first attempt to couple an on-line system to a commercial focused microwave-assisted oven. Only small modifications in this on-line digestion system are necessary to adjust this system to other liquid samples or by using slurry.

Finally, this on-line pointed out the possibility of a more complete mechanization by using solenoid valves and a microcomputer, reducing the action of the analyst.

Acknowledgments

References

1. Simpkins, W.A.; Louie, H.; Wu, M.; Harrison, M.; Goldberg, D.; *Food Chem.* **2000**, *71*, 423.

2. Robards, K.; Antolovich, M.; *Analyst* **1995**, *120*, 1.

3. McHard, J.A.; Winefordner, J.D.; Attaway, J.A.; *J. Agric. Food Chem.* **1976**, *24*, 41.

4. McHard, J.A.; Winefordner, J.D.; Ting, S.; *J. Agric. Food Chem.* **1976**, *24*, 950.

5. McHard, J.A.; Foulk, S.J.; Nikdel, S.; Ullman, A.H.; Pollard, B.D.; Winefordner, J.D.; *Anal. Chem.* **1979**, *51*, 1613.

6. McHard, J.A.; Foulk, S.J.; Winefordner, J.D.; *J. Agric. Food Chem.* **1979**, *27*, 1326.

7. Cohen, E.; Sharon, R.; Volman, L.; Hoenig R.; Saguy, I.; *J. Food Sc.* **1984**, *49*, 987.

8. Cervera, M.L.; Lopez, J.C.; Montoro, R.; *Microchem. J.* **1994**, *49*, 20.

9. Gallignani, M.; Valero, M.; Brunetto, M.R.; Burguera, J.L.; Burguera, M.; Peña, Y.P.; *Talanta* **2000**, *52*, 1015.

10. Wang, Y.; Lu, C.; Xiao, Z.; Kuan, S.S.; Rigsby, E.J.; *J. Agric. Food Chem.* **1991**, *39*, 724.

11. Arruda, M.A.Z.; Gallego, M.; Valcárcel, M.; *Anal. Chem.* **1993**, *65*, 3331.

12. Nikdel, S.; Temelli, C.M.; *Microchem. J.* **1987**, *36*, 240.

13. Rezaaiyan, R.; Nikdel, S.; *J. Food Sci.* **1990**, *55*, 1359.

14. Nikdel, S.; Mackeller, D.G.; Rezaaiyan, R.; *J. Agric. Food Chem.* **1991**, *39*, 1773.

15. Barnes, K.W.; *At. Spectrosc.* **1997**, *18*, 84.

16. Ulrich, N.; *Anal. Chim. Acta* **2000**, *417*, 201.

17. Schwartz, R.S.; Hecking, L.T.; *J. Anal. At. Spectrom.* **1991**, *6*, 637

18. Iyengar, G. V; Subramanian, K. S.; Woittiez, J. R. W.; *Element Analysis of Biological Samples Principles and Practice*, CRC Press: Boca Raton, New York, 1997.

19. Smith, F. E.; Arsenault, E. A.; *Talanta* **1996**, *43*, 1207.

20. Pereira-Filho, E.R; Rohwedder, J.J.R.; Arruda, M.A.Z.; *Analyst* **1998**, *123*, 1023.

21. Pereira, A.V.; Aniceto, C.; Fatibello-Filho, O.; *Analyst* **1998**, *123*, 1011.

22. Burguera, M.; Burguera, J.L.; *Anal. Chim. Acta* **1998**, *366*, 63.

23. Noh, M.F.M.; Hamid, T.A.; Ismail, T.; *At. Spectrosc.* **1998**, *19*, 95.

24. LaFuente, J.M.G.; Marcahnte-Gayon, J.M.; Sanchez, M.L.F.; Sanz-Medel, A.; *Talanta* **1999**, *50*, 207.

25. Pereira-Filho, E.R.; Arruda, M.A.Z.; *Analyst* **1999**, *124*, 1873.

26. Xiang, Y.Q.; Chen, X.G.; Li, G.B.; Hu, Zhao, Z.F.; Hooper, M.; *Lab. Rob. Automation* **2000**, *12*, 91.

27. Neira, J.Y.; Reyes, N.; Nóbrega, J.A.; *Lab. Rob. Automation* **2000**, *12*, 246.

28. Rouseff, R. L., Ting, S. V.; *Citrus Fruits and Their Products: Analysis - Technology*, Marcel Dekker: New York, 1986.

29. Oliveira, A. F.; Fatibello-Filho, O.; *Talanta* **1999**, *50*, 899.

30. Oliveira, A. F.; Fatibello-Filho, O.; Nóbrega, J. A.; *Talanta* **2001**, *55*, 677.

31. Fatibello-Filho, O.; Nóbrega, J. A.; Guaritá-Santos, A. J. M.; *Talanta* **1994**, *41*, 731.