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Automatic flow procedure based on multicommutation exploiting liquid–liquid extraction for spectrophotometric lead determination in plant material

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Abstract

A not expensive automatic flow system based on multicommutation and exploiting the liquid–liquid extraction methodology for the determination of lead in plant material is described. The spectrophotometric procedure for lead determination was based on the reaction with dithizone followed by extraction using an organic solvent. The facilities afforded by the multicommutation approach allowed the use of an air stream as carrier, thus contributing to reduce the overall waste generation. The results obtained analysing plant materials compare very well with those obtained employing inductive coupled plasma optical emission spectrometry (ICP OES) at 90% confidence level. Others profitable features such as a linear response range between 50 and 200 $\mu g\,l^{-1}$ Pb (r = 0.999); a sampling rate of 15 determination per hour; a relative standard deviation of 1.8% (n = 12) for a typical sample containing 163 $\mu g\,l^{-1}$ Pb; a detection limit of 12 $\mu g\,l^{-1}$; a reagent consumption of 4.5 mg dithizone; and a waste generation of 225 μl organic solvent per determination were also achieved.

Keywords: Lead; Multicommutation; Spectrophotometry; Plant material; Liquid–liquid extraction

1. Introduction

The harmful effects on human health caused by lead contamination are well known and among them the lessening caused on enzymatic activities, and kidneys functions and also neuromuscular difficulties have been reported [1,2].

Nowadays there are legal restrictions concerning lead releasing to on the environment. Nevertheless, it is used as a raw material in the manufacturing industry such as automotive batteries, ceramic and ink [3]. Furthermore, lead is a leftover of the some industrial process to produce fertilizer and pesticide. In both case, it could be delivered to the environment either by inadequate manufacturing process or caused by accident.

The plants can absorb lead from the soil, fertilizers and air accumulating in the tissue, thus it can reach the human chain feeding. The lead contamination presents cumulative effect, therefore small concentration could constitute hazard for health if people maintain contact for a long time [2]. In this sense, to assure that foods quality concerning lead contamination, food samples should be periodically analyzed. This monitoring could be a usual practice mainly when plants such as vegetables were produced around industrial zone or when intensive use of fertilizers was employed to improve productivity.

The lead determination in plant material has been carried out using as detection techniques UV–vis spectrophotometry [4], inductive coupled plasma optical emission spectrometry (ICP OES) [5], electrothermal atomic absorption spectrometry [6,7], etc. Among these detection techniques, the UV–vis spectrophotometry requires less expensive equipment. Nevertheless, an extraction step is usually required to improve

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sensitivity, thus increasing the sample handling. In this sense, the time spent to obtain the results is increased mainly if it was used manual procedure. This difficulty has been surmounted employing liquid–liquid extraction or liquid–solid phase extraction approaches using flow injection technique. In this case, high throughput and less reagent and solvent consumption compared with manual procedure have been presented as a main advantage [8–10].

In this work, we intend to develop an automatic liquid–liquid extraction flow procedure for spectrophotometric determination of lead in plant materials. The method selected is that based on the reaction of lead with dithizone followed by an extracting step using an organic solvent prior to detection [11] and the procedure will be implemented employing multicommutation approach [12,13].

Nowadays, there is a claiming concerning environmental quality, thus analytical procedure presenting ability to produce less waste should be appreciated. To attain this requirement the flow system will be designed based on multicommutation [12,13], considering that this approach presents as an inherent feature facility to handle small volume of solutions [14–17]. This feature will be exploited to minimize the consumption of organic solvent, thus contributing to the sustainability of the analytical procedure.

2. Experimental

2.1. Reagents and solutions

All reagents were of analytical grade. Purified water (conductivity < 0.1 $\mu S\,cm^{-1}$) was used throughout.

A 0.01% (w/v) dithizone (H_2Dz) stock solution was prepared by dissolving 10 mg of H_2Dz in 20 ml carbon tetrachloride (CCl_4). After dissolution it was filtered using a Whatman no. 1 filtering paper. A volume of 20 ml ammonium hydroxide solution (dilution 1:50) was added to the vessel containing the filtered H_2Dz. The vessel was shaken and after resting about 2 min, the organic phase was discarded. This step was mandatory in order to remove the products due to dithizone oxidation [11]. The aqueous phase was acidified by adding 10 ml of a 1 mol l^{-1} HCl solution and afterwards, 50 ml of CCl_4 was added to the vessel. The vessel was shaken to permit the H_2Dz transference from aqueous phase to organic phase and after this step, the organic phase presented a green color. The organic phase was transferred to a balloon and the volume was made up to 100 ml with CCl_4. This solution was stored in an amber flask under a layer of a 1 mol l^{-1} H_2SO_4 solution to prevent contact with air and it was maintained in refrigerator. Working solution 0.001% (v/v) dithizone was prepared daily by dilution of dithizone stock solution using CCl_4 as diluting fluid.

A 20% (w/v) hydroxylammonium chloride ($NH_2OH.HCl$) solution and a 20% (w/v) potassium sodium tartrate ($C_4H_4KNaO_6{\cdot}4H_2O$) were prepared by dissolving both solids in water. After dissolution, pH was adjusted to 8.0 using ammonium hydroxide solution. These solutions were purified following the procedure described by Marczenko [11] adding to each one 5 ml of dithizone stock solution described above. After shaking the separation funnel for some seconds it was let to stand rest to allow phase separation. Afterwards, the organic phase was discarded and the solution was stored in polyethylene flask.

Working solution 1.5% (v/v) potassium sodium tartrate plus 0.5% (v/v) hydroxylammonium chloride in a 0.2 mol l^{-1} NH_4OH (pH = 10) medium was prepared using the solutions described in the above paragraph.

A 0.1 mol l^{-1} potassium hexacyanoferrat(II) solution was prepared by dissolving 2.112 g ($K_4[Fe(CN)_6]{\cdot}3H_2O$) salt in 50 ml with water.

A 1000 mg l^{-1} Pb stock solution was prepared by dissolving 1.598 g of $Pb(NO_3)_2$ in water adding to the vessel 1 ml of HNO_3 concentrated. After dissolution the volume was made up to 1000 ml with water.

The working reference solution 0.0, 50.0, 100.0, 150.0, 200.0 and 250.0 mg l^{-1} Pb in a 0.028 mol l^{-1} HNO_3 medium were prepared using a 10.0 mg l^{-1} Pb solution that was prepared before use by appropriated dilution of the Pb stock solution described above.

2.2. Samples preparation

Samples were digested using a microwave-assisted method in closed digesting vessels carried out using an ETHOS 1600 MILLESTONE equipment that was operated as indicated in the manufacturer manual. It was carried out following the sequence: 400 w for 10 min; 600 w for 10 min; 700 w for 30 min. An aliquot of 500 mg dried and powdered plant material (weight carefully) was transferred to the digesting vessel. Before starting the digesting step, 3 ml of a 20% (v/v) HNO_3 solution and 2 ml of a 30% (w/w) H_2O_2 solution were added to the digesting vessel. After decomposition, digesting vessels were cooled, the digestates were transferred to volumetric flasks and the volumes were made up to 50 ml with water.

2.3. Apparatus

The equipment set-up consisted of an IPC-8 Ismatec peristaltic pump equipped with Tygon and Vyton pumping tubes; five three-way solenoids valves (NResearch, 161T031) with barb fitting of polycarbonate; a 432 Femto spectrophotometer (λ = 520 nm) equipped with a lab made glass flow cell, 20 mm optical path, 180 μl inner volume including the two arms; a Pentium III microcomputer equipped with a PCL-711S interface card (American Advantech Corp.); a home made electronic interface as described elsewhere [12] to supply current intensity and voltage required to drive the solenoid valves; a glass separation chamber, with an inner volume of 2.5 ml; and reaction coil and flow lines of polyethylene tubing (0.8 mm i.d.).

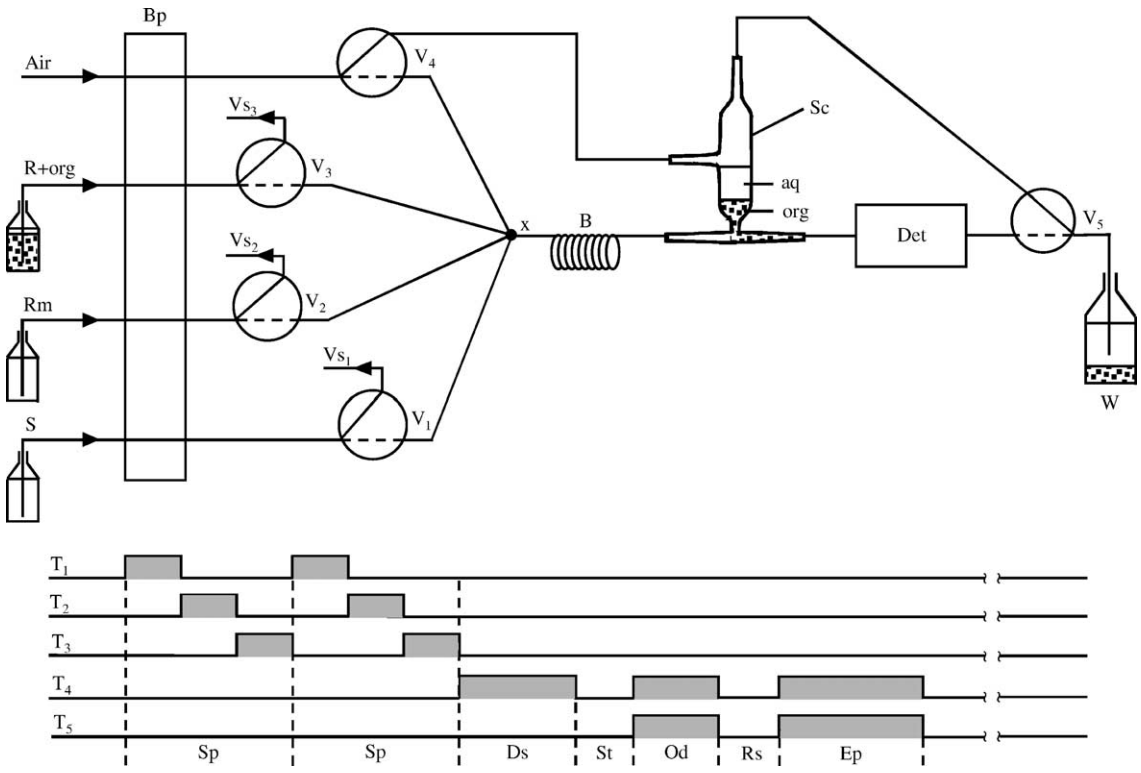

Fig. 1. Diagram of flow of the analysis system. S = sample, flow rate at 3.5 ml min^{-1}; Rm = 1.5% potassium sodium tartrate plus 0.5% (v/v) hydroxylammonium chloride, pH = 10.5, flow rate at 2.9 ml min^{-1}; R + org = 0.001% (w/v) H_2Dz in CCl_4 medium, flow rate at 0.9 ml min^{-1}; Air, flow rate at 6.5 ml min^{-1}; V_1, V_2, . . ., V_5 = three-way solenoid valves; B = reaction coil, 300 cm long, 0.8 mm i.d.; Sc = glass separation chamber, 5 cm height and 1.5 i.d.; Det = spectrophotometer, λ= 520 nm; Vs_1, Vs_2 and Vs_3 = storing vessels; BP = peristaltic pump; x = joint device; W = waste. T_1, T_2, . . ., T_5 = valves timing course, Sp = sampling cycle, Ds = sample zone displacing step, St = phases separation step, Od = organic phase displacing step, Rs = signal reading step, and Ep = separation chamber emptying step. The shadow surface beneath of lines indicated that the associated valve was switched on.

2.4. Flow system and experimental variables

The system manifold was designed to implement the multicommutation approach and its flow diagram is depicted in Fig. 1. In this hardware configuration all valves are switched off and all solutions are pumped back to their storing vessels (Vs_i). The flow system was controlled by a microcomputer running software written in Quick BASIC 4.5. When the software was run, the microcomputer requested the operational parameters summarized in Table 1. Afterwards, the microcomputer sends the set of control signals through the digital output port of the PCL-711S interface card to switch on/off the solenoid valves V_1, V_2 and V_3 following the switching pattern depicted in the valves timing course (Fig. 1). Under this condition, slugs of sample (S), masking reagent (Rm) and organic solvent (R + Org) were inserted alternately into the reaction coil (B). As it is indicated in the valves timing course, two sampling cycles (Sp) were carried out, therefore two sets of slugs (sample, reagent and solvent) were inserted into the reaction coil. After sampling step, these valves were switched off and the displacing step (Ds) was performed switching on valve V_4. While this step was performed, the liquid fluids were pumped back to their storing vessels (Vs_i) and the air stream was directed towards the joint device (x) to displace the sample zone through reaction coil (B) towards the separation chamber (Sc). Mixing between sample and masking reagent solutions and reaction to produce the compound to be detected and extraction occurred during the displacement of the sample zone towards separation chamber (Sc). The displacing time (Ds) was long enough to permit whole sample zone displacement, and also reaction development and extraction. Afterwards, all valves were maintained off for a time interval (St) to allow organic phase separation. While this step was carried out, the air stream flowed through the

Table 1
Valves switching sequence and settled times intervals

Step	V_1	V_2	V_3	V_4	V_5	Time (s)	Volume (μl)
Sample insertion[a]	0	1	0	0	0	1.8	2625
Reagent insertion[a]	0	0	1	0	0	0.5	604
Solvent insertion[a]	0	0	0	1	0	0.6	225
Transport of sample zone	1	0	0	0	0	30	–
Separation step	0	0	0	0	0	20	–
Transport of organic phase	0	0	0	0	1	15.5	–
Signal reading	0	0	0	0	0	15	–
Discard fluid	0	0	0	0	1	45	–

[a] Sequence repeated 25 times. Numbers 1 and 0 indicate valve switched on or off, respectively.

top outlet of the separation chamber (Sc) towards valve V_5. Because the density of the organic phase was higher than that of the aqueous phase, after separation step (St) it fulfills the bottom part of the separation chamber. Afterwards, valve V_5 was switched on (organic phase displacing step, Od). As it is showed in the flow diagram, under this valves configuration, the air stream exerted pressure into the separation chamber, thus causing the displacement of the organic phase towards the spectrophotometer (Det). When the flow cell was filled with organic phase, V_5 was turned off and the data acquisition was accomplished (reading step, Rs) by the microcomputers reading the signal through the analog/digital input of the PCL-711 interface card. Afterwards valve V_5 was switched on (empting step, Ep) to empty both separation chamber (Sc) and flow cell. To avoid the diffusion of the organic solvent vapor (CCl_4) to the laboratory environment a trap of sulfuric acid was used. This was done by adding 5 ml of a 1.0 mol l^{-1} sulfuric acid solution to the bottle containing the organic solvent in order to form a layer (about 5 mm thickness) over organic phase. This protection was possible because the density of the organic solvent was higher that that of the sulfuric acid solution. In the waste vessel the organic phase was maintained under a water layer. To prevent fluid leakage all connection of the flow lines were tighten everyday prior to begin the work. Furthermore, to improve the assurance of the operator the set up was installed into a fume hood.

The volumes of sample and reagents solutions inserted into the reaction coil (B) were defined by the time elapsed while the valves were switched on, therefore the pulsation pattern of the peristaltic pump could cause variation in the loaded solutions volumes. This effect could lessen the precision of measurements, thus to overcome this drawback, the starting of the sampling step was synchronized with pumping pulsation as described earlier [10].

The fluids pumping rates described in the legend of Fig. 1 were maintained throughout. Unless specified, the experiments described below were carried out using reference solution presenting concentration within the range 50–400 μg l^{-1} Pb and performing 25 sampling cycles (Sp). The system variables assayed were reaction coil length, time interval to switch valves, reagents concentration and pH.

The reaction coil effect on the reaction development and extraction was the first parameter assayed by changing its length from 150 to 450 cm. The volumes of the solutions aliquots were varied controlling the time interval elapsed while the related valve was maintained switched on. In this sense, the time intervals to switch on valves V_1, V_2 and V_3 were varied from 1.0 to 1.8, 0.3 to 0.7 and 0.4 to 1.3 s, respectively.

The studies concerning to reagents concentrations and pH effect were carried out by varying their concentrations between 1×10^{-4} and 5×10^{-3}% (v/v) dithizone, 1.0 and 2.5% (v/v) potassium sodium tartrate and 0.5 and 1.5% (v/v) hydroxylammonium chloride. The assays were repeated varying the pH from 8.5 to 11.

Complementary assays were performed to verify the ability of the $K_4[Fe(CN)_6]$ as masking reagent to overcome the interferences that could be caused by the concomitant ions such as Ag, Cd, Co, Cu, Ni, Sn and Zn, which could be found in the sample solution. The experiments were carried out using lead reference solutions with and without these cations. This assay was performed using a 0.1 mol l^{-1} $K_4[Fe(CN)_6]$ solution and adding 1.0–50.0 ml of standard solution containing Ag, Cd, Co, Cu, Ni, Sn and Zn.

To demonstrated the usefulness of the proposed system a set of samples comprising different vegetables were analyzed using the experimental variables summarized in Table 1. Prior to analysis, a 500 μl aliquot of the 0.1 mol l^{-1} $K_4[Fe(CN)_6]$ solution was added to 25 ml of the sample solution. To allow data comparison the samples were also analyzed employing the inductively coupled plasma optical emission spectrometry (ICP OES).

3. Results and discussion

3.1. Effect of the reaction coil length

Because the length of the reaction could affect analytical signal concerning to precision and sensitivity, assays were carried out using reaction coils presenting lengths of 150, 300 and 450 cm. The results obtained with reaction of 300 and 450 cm were similar in sensitivity and linearity (R = 0.998). By another hand, the results obtained with reaction coil of 150 cm were worse in sensibility (ca 40% less) and in linearity (R = 0.985). The experiments were carried out using reference solutions presenting concentration between 100 and 400 μg l^{-1} Pb. The chromogenic reagent was dissolved in the organic phase, therefore the reaction to form the Pb–dithizone compound was dependant of lead ions migration from the aqueous phase to the organic phase. The results indicated that this effect was improved by increasing the reaction coil length. Once results were similar the reaction coil presenting length of 300 cm was selected aiming to improve the throughput.

3.2. Effects of sample volume and reagent concentration

The liquid–liquid extraction implemented using a flow system can present a direct relationship concerning the signal magnitude and the ratio between the volumes of the aqueous and the organic phases. In this sense, the sensibility of the procedure could be improved by controlling the ratio between the volumes of the sample solution and of the organic phase. This possibility was investigated maintaining the volume of the extracting fluid at 225 μl. The time interval to switch on valve V_1 was varied from 1.0 to 1.8 s performing 25 sampling cycles. The measurements were processed applying a linear regression treatment yielding the results showed in Table 2.

Comparing the slopes of the analytical curves obtained using the lower and higher sample solution volumes, we can

Table 2
Linear curve fitting parameters (n = 3)

Sample volume (μl)	Slope (α)	Linear correlation coefficient (R)	Blank measurement/ intercept (mV)
1425	439.5	0.998	−18.3 ± 0.4
1750	479.7	0.996	−13.2 ± 0.8
2041	617.7	0.999	−14.9 ± 1.3
2333	576.9	0.997	−15.7 ± 0.2
2625	689.7	0.999	−19.3 ± 0.8

deduce that an increase in signal about of 56% was obtained. These results show that the increasing of the sample volume is a strategy that should be considered to improve sensitivity. The blank measurements presented similar values in the five cases, thus indicating absence of contamination. This effect could be identified as a notable advantage, considering that an increase of the blank measurements could become a limiting factor of the procedure.

Dithizone was dissolved in the organic phase and its volume was maintained at 225 μl. Under this condition, the assays to find the amount of the reagent necessary to assure an adequate condition for the chemical reaction development were carried out varying its concentration, yielding the results showed in Table 3. The worst results are those related to dithizone concentration of 0.0001% (v/v). Once the results obtained at the other two reagent concentrations were similar, the concentration of 0.001% (v/v) dithizone was selected.

3.3. pH effect

The effect of the pH on the reaction was verified by using potassium sodium tartrate/hydroxylammonium chloride solutions presenting pH between 8.5 and 11.0. The results obtained using solutions with pH 8.5 and 9.0 showed no significant difference between measurements of the blank and of a solution containing 400 $\mu g\,l^{-1}$Pb. At part from the results obtained using solution with higher pH were derived the parameters values showed in Table 4. As it can be seen, the better results were achieved using solution of pH 10.0. The lower measurement value of the blank solution constituted a favourable factor, inasmuch as a high value could cause a diminution of the linear response range of the procedure. In this sense, the solution of pH 10.0 was selected.

The results showed in Table 4 indicated that pH variation could worsen the precision of the results. Because plant material was mineralised using an acid medium, assays using Pb reference solutions prepared in 0.014, 0.028 and 0.14 $mol\,l^{-1}$ HNO_3 medium were carried out in order to define the acid concentration of the samples solution. The analytical curves using reference solutions with acid concentration of 0.014 and 0.028 $mol\,l^{-1}$ HNO_3 were similar. By other hand, the results obtained using the higher concentrated acid solution were worse; no significant difference between blank and reference solution signals was observed. Considering these results, after sample mineralising, the acid concentration was adjusted to 0.028 $mol\,l^{-1}$ HNO_3.

Table 3
Effect of dithizone concentration

Parameter	Dithizone 0.0001% (v/v)	Dithizone 0.001% (v/v)	Dithizone 0.005% (v/v)
Linear response coefficient (R)	0.987	0.998	0.997
Slope ($mV/\mu g\,l^{-1}$)	0.186	0.761	0.728
Relative standard deviation, RSD (%)	1.9	2.3	3.1

Table 4
Effect of the pH on the system response

Parameter evaluated	pH 9.5	pH 10.0	pH 10.5	pH 11.0
Linear response coefficient (R)	0.998	0.999	0.999	0.991
Slope ($mV/\mu g\,l^{-1}$)	0.602	0.852	0.671	0.662
Relative standard deviation, RSD (%)	2.6	1.2	1.8	6.1
Blank measurement (mV)	109.1	59.8	80.8	97.8

3.4. Interference suppressing

Previous assays indicated that the interference effects caused by several metal ions (Ag, Cd, Co, Ni, Cu, Sn, Zn) naturally existing in plant material were not effectively suppressed by the masking solution comprising potassium sodium tartrate/hydroxylammonium chloride. To overcome this drawback usually cyanate had been used as masking reagent [18,19]. Albeit its ability as masking is recognized, careful manipulation is required mainly when the sample to be processed must be mineralised in acidic medium such as plant material. In this sense, following an indication pointed out by Klinghoffer et al. [20] we decided to use a 0.1 $mol\,l^{-1}$ $K_4[Fe(CN)_6]$ as a masking solution. According to the results showed in Table 5, the interfering effects concerning this set of ions were reduced to acceptable values. The ions concentrations used in these assays were higher than those usually found in plant material.

Table 5
Interference suppressing using $K_4[Fe(CN)_6]$ (n = 3)

Pb + interfering ion ($mg\,l^{-1}$)	Signal (mV)	
	Without masking solution	With masking solution
Blank	116.1 ± 1.0	93.0 ± 1.0
0.1	189.0 ± 1.2	141.3 ± 1.0
0.1 + 1.0 (Ag)	111.1 ± 1.3	140.5 ± 1.3
0.1 + 1.0 (Cd)	364.1 ± 2.4	142.1 ± 1.6
0.1 + 1.0 (Co)	237.3 ± 2.4	136.9 ± 2.2
0.1 + 5.0 (Cu)	473.6 ± 2.6	143.7 ± 1.0
0.1 + 1.0 (Ni)	156.4 ± 1.2	147.0 ± 2.1
0.1 + 0.5 (Sn)	192.7 ± 1.9	142.1 ± 1.1
0.1 + 5.0 (Zn)	343.8 ± 2.9	145.3 ± 2.1

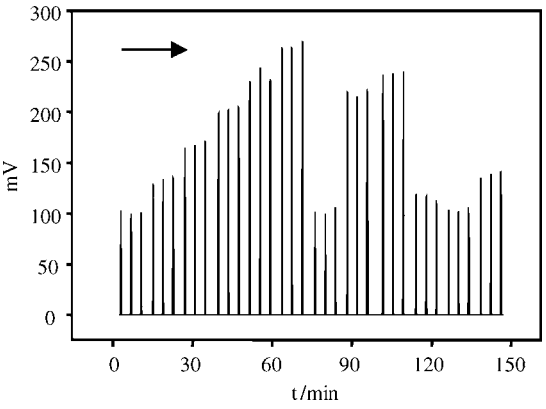

Fig. 2. Records of an analytical run. From right records in triplicates: 0.0, 50.0, 100.0, 150.0, 200.0 and 250.0 mg l^{-1} Pb followed by a set of six samples. In the set up used the mV relationship to absorbance was 0.1 uA to 60 mV.

3.5. Sample analysis

Considering the results discussed in the previous sections, additional experiments were carried out using the system parameters summarized in Table 1. Standard solutions and plant digests were processed yielding the results displayed in Fig. 2. By processing the measurements of the reference solutions a linear relationship, mV = 101.57 ± 1.65 + (0.76 ± 0.01) mg l^{-1} Pb (R = 0.999) was achieved, thus indicating that the system parameters of Table 1 can be used to obtain analytical results. As it can be seen, the repeatability of the records is comparable with those observed in usual FIA system. No drift of baseline is also observed, thus confirming that the system is very stable. From these Fig. 1 can deduce that a sampling rate of 15 determinations per hour was achieved.

Aiming to demonstrate the usefulness of the proposed system, acid digests of samples comprising vegetables and certified material were analyzed. To permit results comparison sample solution were also analyzed employing inductively coupled plasma optical emission spectrometry (ICP OES). Results obtained are shown in Table 6. Applying the t-test for multiples samples no significant deference at 90% confidence level was observed. Others profitable features such as a linear response ranging from 50 to 200 μg l^{-1} Pb (r = 0.999); a sampling rate of 15 determination per hour; a relative standard deviation of 1.8% (n = 12) for a typical sample containing 163 μg l^{-1} Pb; a detection limit of 12 μg l^{-1}; and a reagent consumption and a waste generation of 4.5 mg dithizone and of 225 μl organic solvent per determination, respectively, were also achieved.

Table 6
Results comparison (n = 3)

Samples	Proposed procedure (mg kg^{-1}) Pb ± S.D.	Spectrometry (ICP OES) (mg kg^{-1}) Pb ± S.D.
Aubergine	12.87 ± 0.06	13.33 ± 0.20
Grass 1	4.55 ± 0.10	4.49 ± 0.19
Grass 2	1.62 ± 0.10	1.52 ± 0.15
Lettuce 1	16.37 ± 0.37	16.63 ± 0.15
Lettuce 2	20.48 ± 0.59	20.71 ± 0.29
Pumpkin	9.99 ± 0.19	9.58 ± 1.11
Peach leaves (0.87 ± 0.03)[a]	0.95 ± 0.14	–
Rye grass (2.38 ± 0.11)[a]	2.25 ± 0.12	–

[a] Certified materials and the numbers between parentheses are the certified values (mg kg^{-1}) Pb ± the confidence interval.

4. Conclusion

The processed sample zone was stopped into the flow cell to carry out dada acquisition, thus this strategy presented as an advantage the decrease of organic phase volume.

The analytical procedure presented a good robustness and operational facilities that was implemented using no expensive instrumentation. This is an association so difficulty to be achieved.

In the usual flow system, the carrier solution generally is the major contributor to the waste generation. In this work, it was use an air stream as carrier fluid, thus contributing to reduce the volume of waste generated. This arrangement could be considered as an improvement compared with previous work where an acid solution was used as carrier stream [10].

The system manifold based on multicommutation permitted the easily handling the three fluids phases in the system: aqueous sample and masking solution, organic extracting, and air stream.

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