Simultaneous Determination of Potassium and Sodium in Vegetables by Flame Emission Spectrometry Using a Flow-Injection System with Two Dialysis Units

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A flow-injection (FIA) manifold is described for the simultaneous determination of potassium and sodium in samples of vegetables using flame emission spectrometry as the detection process. Two dialysis units were included so as to provide the system with a high dilution capacity (dilutions of about 600 – 700 fold), and also to allow bicomponent analysis: the same sample plug was divided between a donor and an acceptor stream that were subsequently directed to two detectors placed in parallel. The results of the FIA method were in good agreement with those of the reference procedures (relative deviations lower than 3%). Sampling rates from 120 to 150 samples per hour (corresponding to 240 to 300 determinations per hour) were achieved with relative standard deviations below 1.7%.

Keywords Multidetection, flow injection analysis, dialysis, sodium, potassium, vegetables, flame emission spectrometry

Potassium and sodium determinations in plant materials are usually accomplished by atomic absorption and/or flame emission spectrometry methodologies.[1-3] The overall process is rather time-consuming, involving sample digestion and subsequent adjustment of the digest composition to the requirements of the detection system. If flame emission spectrometry is used, the preparation of the digests implies their dilution in order to fit the sample analyte content to the linear working range. Since the sodium and potassium contents in plants may present a large range of concentrations, a trial-and-error approach must be used, thus making the dilution step a very tedious and slow process. The use of flow injection analysis to automate the sample dilution process and the introduction in the detector would thus be advantageous to considerably decrease the analysis time. The FIA manifold analytical capacity would still be enhanced if the set-up could be designed so as to allow the determination of both analytes over the same injected sample.

Some FIA manifolds have already been described for analyzing cationic species in soils, wines, water and plants by atomic absorption or emission spectrometry, in which automatic sample dilution was performed by controlling such manifold parameters as the injection volume, flow-rates, tube lengths and overpressure at the nebulizer entry.[4-9] However, when high sample in-line dilutions must be obtained, the use of dialysis units has proven to be a very efficient and a simple way to achieve it.[8-11] Due to the low efficiency of the process (the amount of analyte that diffuses from a donor to an acceptor stream driven by the concentration gradient is quite reduced), large dilutions are easily accomplished with a high sampling rate. Moreover, simultaneous determinations are feasible because the injected sample is separated in the dialyzer unit between two channels (donor and acceptor) that may then be directed to different detectors placed in parallel.[8-10]

In this work a flow-injection manifold which incorporates two dialysis units in series is described; it performs the simultaneous determination of potassium and sodium in digests of vegetables by flame emission spectrometry. The quality of the obtained results with the developed FIA methodology was assessed by a comparison with those given by conventional FES procedures.[3]

Experimental

Reagents and solutions

Deionized water (conductivity lower than 0.1 μS cm^{-1}) and analytical reagent-grade chemicals were used for the preparation of all the solutions.

Potassium (10000 mg l^{-1}) and sodium (5000 mg l^{-1}) stock solutions were prepared by precisely weighing previously dried (at 100°C for over an hour) solid KCl and NaCl, and were then dissolved in 0.4 M HCl. The

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working standards for flow-injection measurements and reference procedures were obtained by a rigorous dilution of the stock solutions in 0.4 M HCl and water, respectively.

Instrumentation

Potassium determinations were carried out in a Corning (Model 410) flame emission spectrometer; those of sodium were analyzed in a Buck Scientific (Model PFP-7) flame photometer, using air–propane flames. Both of the detectors were connected to a double-channel (Kipp & Zonnen BD 112) chart recorder for a simultaneous registration of the two analytical signals.

Flow-injection manifold

In the FIA system the solutions were propelled by a Gilson Minipuls 3 peristaltic pump and propulsion tubes of the same brand. Standards and digests of vegetables were introduced with a Rheodyne (Type 50) injection valve.

Omnifit Teflon tubes (0.8 mm i.d.) along with Gilson end-fittings and connectors were used to link the different manifold components.

The two dialysis units, having a configuration similar to one previously described[11] had a flow channel 2 mm wide and 0.5 mm deep, and linear path lengths of 35 mm and 70 mm. These units were made of perspex and comprised two half blocks, pressed against each other by four screws. A Tecator (ref. 5588 0002) dialysis membrane was placed between the two blocks (separating the donor and acceptor streams) and kept in contact with water between determinations in order to allow measurements immediately after starting up the FIA system. The membrane was replaced whenever a signal decrease was observed for consecutive injections of the same solution. In order to obtain good reproducibility, the membranes were conditioned in deionized water (by circulating water on both the donor and acceptor channels at a low flow-rate) for at least one hour before their first use.

Vegetable sample preparation

Five samples of each vegetable (lettuce, spinach, parsley, watercress, turnip leaf and turnip sprouts) were oven dried (at 80 – 100°C) and their particle size was reduced by grinding using a moving-blade mill. For both reference methods and FIA determinations, digests of the vegetables were prepared by wet acid digestion[2], as follows: 2 g of each dried sample was mixed with 30 ml of digestion acid (1 vol. $HClO_4$ 60% : 4 vol. HNO_3 70%) in a borosilicate glass beaker (tall form with a spout) and allowed to stand overnight at room temperature. The resulting solution was placed on a thermostatically controlled hotplate, and the temperature was maintained at 100°C for approximately 2 h. After that time, the temperature was first increased to 180 – 200°C and then to 240°C; the heating was continued until a dry residue was obtained. When cool, 10 ml of 2 M HCl was added; the solution was then gently heated for approximately 5 min. The digest was quantitatively transferred to a 50 ml volumetric flask; after cooling the volume was completed with deionized water. At last, samples were filtered through Whatman (No. 541) filter paper into polyethylene bottles and stored at 4°C until use.

Reference procedures

For comparison purposes, sodium and potassium determinations were carried out over diluted digests of vegetables using flame emission spectrometry as the detection process.[3] The standards were first introduced in the flame photometer in order to establish calibration curves. The digests of vegetable were then diluted by a trial-and-error approach in order to fit their concentration within the linear range of each calibration plot. Afterwards they were introduced into the flame photometer and the concentrations were obtained from the calibration curve. At least two replicates were prepared and analyzed for each sample.

Results and Discussion

Flow-injection manifold

The configuration of the FIA system was designed so as to achieve two goals: (i) to obtain two plugs from the same injected sample and then to direct them to different flame photometers placed in parallel, in order to allow a simultaneous analysis; (ii) to carry out high in-line dilutions of the sample digests in order to allow measurements in a linear dependence range for the sodium and potassium determinations. These objectives were made possible by placing two dialysis units in series in the flow system, as depicted in Fig. 1.

The sample is first injected in a water carrier stream (donor channel) and then driven to a dialysis unit (D_1) located after the injection point. The ions diffuse to the acceptor channel across the membrane (driven by the concentration gradient) and the dialyzate is directed to the flame emission detector for a potassium determination. The undialyzed plug, which remains almost unaltered, moves forward to the next dialyzer (D_2) where a new diffusion process takes place and a new dialyzate is formed, which allows a determination of sodium in the digests of vegetables. Therefore, the high in-line dilutions needed before instrumental measurements were achieved in a simple and precise manner due to the low yield of the dialysis process. Since the potassium concentration in plants is generally higher than that of sodium[4–6,12–14] (the same occurring with samples of analyzed vegetables whose K and Na concentrations were determined by conventional FES procedures before the development of the manifold), a smaller dialysis unit (3.5 cm long) was chosen for the K determinations, because the efficiency of the dialysis process is inversely proportional to the channel dimensions. For sodium determination a 7 cm long dialysis unit was used. Since the natural aspiration rate of the spectrometers used was approximately 4.8 ml min^{-1}, the flow-rate of the three

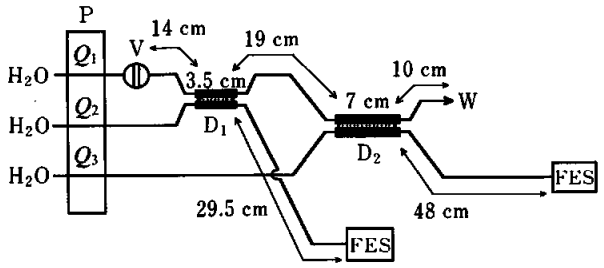

Fig. 1 Flow-injection manifold developed for the simultaneous determination of potassium and sodium by flame emission spectrometry in samples of vegetables: P, peristaltic pump; V, injection valve (278 µl); Q_i, flow-rates (5.0 ml min^{-1}); D_i, dialysis units; FES, flame emission spectrometers; W, waste.

channels was set to 5.0 ml min^{-1}. Under such conditions, the flow-rate entry in the nebulizers was controlled by the peristaltic pump, not by the aspiration system of the detector, thus attaining a better precision in the measurements.

Regarding the preparation of flow-injection standard solutions, since the digests of vegetables were acidic solutions (total acidity of the digests ranged from 0.35 to 0.59 M) and since the H^+ ion is known to cause difficulty regarding the transport and charge balance between the two streams of the dialysis units[8–10] it became necessary to acidify the working standards so as to match the transport process across the membrane for the samples and standards. To study the influence of the proton concentration, a set of standard solutions of K, Na and K/Na (with different K/Na ratios) were prepared in deionized water and HCl solutions with concentrations of 0.4, 0.5 and 0.6 M. Upon comparing the peak heights for the K, Na and K/Na standards prepared in hydrochloric acid with those obtained for solutions with the same analyte concentrations prepared in water, a notorious decrease was found. Yet, similar heights were obtained for all of the standards prepared with different acid concentrations (the differences were always lower than 10%). The HCl concentration in the standard solutions was then set to 0.4 M and mixed (K/Na) standards were used throughout in FIA determinations.

Table 1 Potassium and sodium concentrations (expressed in milligrams of analyte per gram of dried sample) of 30 digests of vegetables obtained by flowinjection analysis (C_f) and by reference procedures (C_r)

Sample		Potassium			Sodium		
		C_f/mg g^{-1}	C_r/mg g^{-1}	RD[a], %	C_f/mg g^{-1}	C_r/mg g^{-1}	RD[a], %
Watercress	1	35.7	35.7	0	15.7	16.0	−1.9
	2	38.9	38.8	0.26	7.58	7.58	0
	3	33.8	34.0	−0.59	11.4	11.4	0
	4	28.6	27.9	2.5	8.37	8.31	0.72
	5	32.4	32.4	0	8.93	9.04	−1.2
Lettuce	1	48.8	48.8	0	1.19	1.19	0
	2	43.7	44.2	−1.1	4.65	4.65	0
	3	55.9	55.8	0.18	2.18	2.18	0
	4	52.2	52.2	0	3.17	3.16	0.32
	5	54.9	54.8	0.18	4.63	4.57	1.31
Spinach	1	26.1	26.1	0	32.2	32.2	0
	2	29.7	29.8	−0.34	27.7	27.6	0.36
	3	25.8	26.1	−1.1	25.4	25.2	0.79
	4	36.6	37.2	−1.6	17.7	17.3	2.3
	5	25.3	25.4	−0.39	44.1	44.2	−0.23
Turnip sprout	1	33.8	34.0	−0.59	2.19	2.19	0
	2	32.3	32.3	0	3.59	3.61	−0.55
	3	32.9	32.9	0	2.43	2.43	0
	4	40.1	39.6	1.3	2.24	2.24	0
	5	34.0	34.0	−0.33	2.28	2.28	0
Turnip leaf	1	42.7	43.0	−0.70	15.9	15.9	0
	2	42.6	42.6	0	8.05	8.05	0
	3	66.0	67.7	−2.5	4.46	4.45	0.22
	4	53.2	51.7	2.9	10.0	10.0	0
	5	46.9	46.9	0	5.09	5.09	0
Parsley	1	33.5	34.0	−1.5	7.85	7.80	0.64
	2	38.5	38.6	−0.26	6.77	6.77	0
	3	51.4	52.1	−1.3	5.97	5.80	2.9
	4	37.3	37.3	0	5.71	5.83	−2.1
	5	34.4	33.5	2.7	5.23	5.17	1.2

a. Relative deviations.

Table 2 Comparison of the results obtained in the digests of vegetables determinations by the developed bicomponent FIA system (C_f) and by the reference procedures (C_r): relative standard deviations, dispersion levels and sampling rates achieved with the FIA manifold used

	Equation parameters ($C_f=C_0+SC_r$)			Number of samples analyzed	Characteristics of the FIA system		
	C_0/mg g^{-1}	S	R^a		RSD^b, %	Dispersion coefficient	Sampling rate (samples h^{-1})
Potassium	0.5	0.987	0.999	30	<1.6	687	120 - 150
Sodium	0.01	1.00	1	30	<1.7	591	120 - 150

a. Correlation coefficient. b. Relative standard deviation obtained from 10 consecutive injections of vegetable digests.

Some assays were then carried out in order to establish the injection volume to be used in bicomponent analyses of the samples. An injection volume of 278 µl was chosen. Lower injection volumes (189 and 222 µl) produced lower sensitivity measurements, while a higher volume (337 µl) produced only a slight increase in the signal magnitude and sensitivity, and had the disadvantage of increasing the time to return to the baseline.

With these preset parameters the dispersion coefficient was 687 for the potassium determination and 591 for the sodium determination, calculated as the ratio between the concentration before the introduction in the flow system and the maximum concentration at the moment of detection. The working linear concentration range for K and Na determinations were also assessed: the lower limit corresponds to the methodology detection limit, calculated as the concentration corresponding to three-times the standard deviation of the system background noise, while the upper limit was estimated from calibration plots. Using this manifold, it is possible to analyze samples containing between 24.6 mg l^{-1} (0.00107 M) and 2.30×10^2 mg l^{-1} (0.100 M) of sodium and between 60.6 mg l^{-1} (0.00155 M) and 14.7×10^3 mg l^{-1} (0.375 M) of potassium.

Determination of potassium and sodium in vegetables

The developed FIA manifold was used for sequential determination of potassium and sodium in 30 samples of 6 different vegetables (Table 1). The results are expressed as milligrams of analyte per gram of dried sample of vegetable.

The digests were injected into the manifold without any former treatment, being the concentration calculated by interpolation in previously established calibration plots (Fig. 2).

The quality of the results obtained by the FIA (C_f) methods was evaluated by comparing them with those provided by reference procedures (C_r), in which the samples were prepared in a discrete manner; afterwards the analyte concentration was measured using the same detection systems in a conventional manner. With this set of values, a relationship of the type $C_f=C_0+SC_r$ was established for both cationic species (Table 2). A good agreement was obtained between the two methodologies, as can be perceived by the slope and intercept values.

To establish the precision of the FIA methodology,

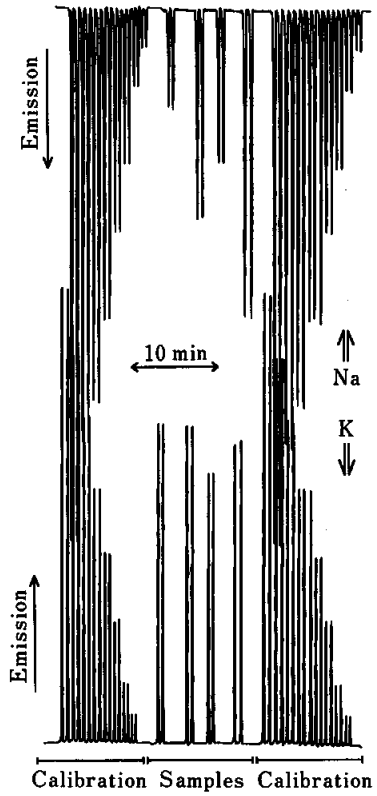

Fig. 2 Recorder output obtained for the simultaneous determination of potassium and sodium in digests of vegetables using two flame emission spectrometers as detection systems. The concentrations of the injected standard solutions ranged from 206.4 to 2896 mg l^{-1} for potassium and between 81.02 to 1158 mg l^{-1} for sodium.

relative standard deviations were determined from ten consecutive injections of several samples of vegetables with concentrations covering the analytical range found for each determination (the reproducibility for K analysis was evaluated using 4 sample digests with concentrations of between 31 and 55 mg g^{-1}, while Na reproducibility was evaluated using 7 samples with concentrations of between 2.3 and 16 mg g^{-1}). The relative standard deviations observed were always lower than 1.7% (Table 2).

Sampling-rates in the 120 to 150 samples h^{-1} range (*i.e.* 240 - 300 determinations per hour) were achieved,

depending on the concentration level of the samples.

In conclusion, the developed FIA methodology is a good alternative to the conventional procedures for potassium and sodium determination in vegetable samples. It allows in-line preparation of the digests for the instrumental measurement as well as simultaneous analysis of both analytes, with high sampling rates and good reproducibility.

The system is good for routine analyses, since it requires little maintenance and makes use of the same detection system employed for the reference methods.

It is still worthy to point out that an additional determination could be done if the sample bolus contained in the donor stream (carrier stream) was directed to a third detection system. Moreover, if this detector was non-destructive a fourth determination could be performed afterwards.

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