

Flow Injection Determination of Sodium, Potassium, Calcium, and Magnesium in Beer by Flame Emission and Atomic Absorption Spectrometry

Sílvia M. V. Fernandes and António O. S. S. Rangel*

Escola Superior de Biotecnologia, Universidade Católica Portuguesa,
Rua Dr. António Bernardino de Almeida, 4200 Porto, Portugal

José L. F. C. Lima

CEQUP/Departamento de Química-Física, Faculdade de Farmácia,
Rua Aníbal Cunha 164, 4050 Porto, Portugal

Flow injection systems for the determination of sodium and potassium, by flame emission photometry, and calcium and magnesium, by atomic absorption spectrometry, in beer are described. The samples were directly injected in the flow system where automatic dilution occurred, and reagent addition using the merging zones technique was performed. Lanthanum(III) consumption was reduced in about 20–80-fold compared to conventional manual atomic absorption determinations. Sampling rates of 120–200 determinations/h were achieved. The results were in agreement with the reference procedures (relative deviations below 3.8%) and present good reproducibility (relative standard deviations lower than 1.6% for 10 consecutive measurements).

Keywords: *Flow injection; beer; Na; K; Ca; Mg; flame emission; atomic absorption spectrometry*

INTRODUCTION

The flavor and stability of beer is greatly influenced by the quantity and nature of the dissolved cations and their reactions with the various constituents of malt and hops (Buckee, 1991), thus justifying their determination for routine quality control in breweries. Calcium and magnesium ions in beer act as cofactors for certain enzymes (Charalambous and Bruckner, 1977) that are active during fermentation. It has also been reported (Buckee, 1991) that the presence of magnesium in considerable amounts can have an adverse effect on flavor, e.g., in terms of producing a more astringent bitterness. Sodium and potassium ions impart a salty and sour taste to beer (Buckee, 1991). The concentrations of these metallic ions in beers (Hough et al., 1982) can range from 9 to 230 ppm for sodium, 220 to 1100 ppm for potassium, 4 to 135 ppm for calcium, and 34 to 250 ppm for magnesium.

The determination of these analytes has been generally accomplished by flame emission (sodium and potassium) and atomic absorption spectrometry (calcium and magnesium). The measurement procedures by these methods are simple and quick. However, before sample introduction into the flame atomization system, it is necessary to fit its composition to the instrumental demands. This includes dilution of the samples to allow determinations in a linear dependence range and to minimize matrix physical interferences and, in the case of calcium and magnesium, the addition of a releasing agent to eliminate chemical interferences. As these necessary steps for sample preparation are often laborious and very time consuming, they generally limit the overall analysis time and make automation advantageous.

In this paper, two different flow injection analysis (FIA) systems for the determination of metallic cations in beer are presented. In order to obtain a dilution capacity necessary for a set of determinations, a flow manifold with either a stream splitting and a detector inlet overpressure or a dialysis unit (Ferreira et al.,

1995) were devised. The use of a flow splitting can be an efficient way to increase dilution by reducing the amount of analyte that is led to the flame atomization system. To obtain a further decrease in the analytical signal, the nebulization efficiency was reduced by imposing a flow rate at the nebulizer entry higher than the uptake rate of the detector. A manifold with a dialysis unit was used to achieve a higher dilution capacity. Due to the low efficiency of the diffusion across the membrane from a donor to an acceptor channel, a large reduction in the amount of analyte reaching the detector is achieved.

The addition of the releasing reagent in the calcium and magnesium determinations was carried out by resorting to the merging zones technique (Bergamin et al., 1978). This flow injection mode has been used to reduce reagent consumption, as only the required amount for the reaction is introduced in the system instead of its continuous flow through the manifold. In this work, advantage was taken from this principle to minimize lanthanum(III) consumption, as it is an expensive reagent.

MATERIALS AND METHODS

Reagents and Solutions. All chemicals were of analytical reagent grade, and deionized water with a specific conductance less than $0.1 \mu\text{S cm}^{-1}$ was used throughout.

The standard solutions used in the establishment of the flow injection calibration graphs of calcium (40–160 ppm) and magnesium (20–160 ppm) were prepared by rigorous dilution of BDH Chemicals standard solutions of 1000 ppm. The sodium and potassium 1000 ppm stock solutions were prepared by precise weighing of previously dried (at 100°C) solid sodium chloride and potassium chloride, respectively. Working standard solutions containing sodium in the range 10–130 ppm and potassium in the range 100–500 ppm were prepared by rigorous dilution of each stock solution in water.

The 0.3 M nitric acid solution was prepared by dilution of concentrated nitric acid ($d = 1.52$; 100%) in water.

The lanthanum(III) stock solution used for the calcium and magnesium determinations was prepared from solid La_2O_3 and

presented a final concentration of 50 000 ppm in lanthanum(III) and 3 M in HCl. Working FIA 10 000 ppm lanthanum(III) solution was prepared by dilution of the stock solution. Beer samples were degassed in an ultrasonic bath for 10 min prior to their introduction in the FIA system.

Reference Manual Procedures. For comparison purposes, sodium and potassium were determined by flame emission spectrometry, and calcium and magnesium by atomic absorption spectrometry, in diluted beer samples. Calibration curves were established in the range 0.1–1 ppm for sodium, 2–10 ppm for potassium, 0.5–2.5 for calcium, and 0.05–0.5 for magnesium. The beer samples were diluted in 50 mL volumetric flasks by a trial-and-error approach, in order to fit their concentration within the linear range of each calibration plot. In the calcium and magnesium determinations, standards and samples presented a lanthanum(III) concentration of 10 000 ppm.

Apparatus and Flow Injection System. Flame emission determinations of sodium and potassium were carried out using a Corning 410 flame photometer with an air–propane flame. A GBC 902 atomic absorption spectrophotometer with an air–acetylene flame was used for the determination of calcium and magnesium. Both instruments were coupled to a Kipp & Zonen BD 111 chart recorder.

In the flow injection systems, the solutions were propelled by Gilson Minipuls 2 and Minipuls 3 peristaltic pumps and PVC Gilson propelling tubes; the tubes were replaced when the flow stability decreased, yielding flow pulses and consequently nonreproducible signals. The solutions were injected in the manifolds with Rheodyne type 5020 six-port rotary valves. For calcium and magnesium determinations, two valves were connected by a metallic axle (Fernandes et al., 1995) so that the switching of the valve positions occurred at the same time, thus allowing the simultaneous injection of samples or standards and lanthanum(III) solution. Omnifit PTFE tubing (0.8 mm i.d.) with Gilson end fittings and connectors and Perspex homemade Y-shaped joints were used as confluence or stream-splitting points. The homemade dialysis unit incorporated in the manifold for the determination of magnesium was made of Perspex (Lima et al., 1994). It consisted of two separate blocks, pressed against each other by eight screws. The matching cavities drilled in each block were 2 mm wide, 0.5 mm deep, and 7 cm long (linear path). The membrane placed between the two blocks was Tecator reference 5588 0002.

RESULTS AND DISCUSSION

The concentration of sodium, potassium, calcium, and magnesium in beer is usually much higher than the working linear concentration ranges of the detection systems used. Flow injection manifolds were therefore developed to perform automatically the dilution, reagent addition, and introduction of beer samples into the detection systems. Two FIA manifolds were devised, each one presenting different dilution capacities. The required dispersion levels for calcium, sodium, and potassium determinations were achieved by the joint effect of a confluence stream and a stream splitting, while higher dilutions were obtained by using a dialysis unit (determination of magnesium).

Determination of Calcium, Sodium, and Potassium. In order to develop a FIA system to provide the required sample treatments, a manifold was assembled (Figure 1) consisting of a three-channel system with a confluence point (Y) placed after a stream splitting (X). Additionally, for calcium determination, it was necessary to add the lanthanum(III) reagent, which was made by the merging zones technique, in order to save lanthanum solution.

The flow system was designed so that it could be used for the determination of Ca, Na, and K without needing significant changes in the manifold. The optimization

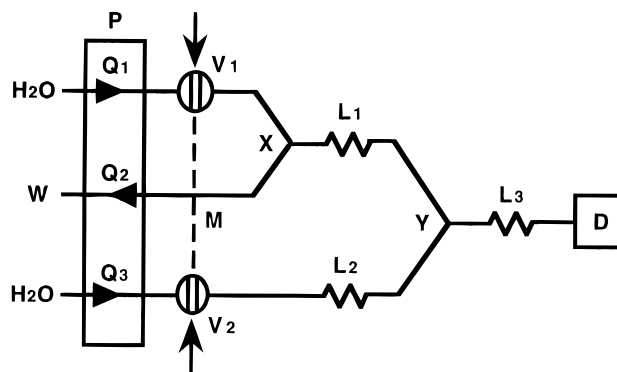


Figure 1. Flow injection manifold developed for the determination of calcium, sodium, and potassium in beer: D, detector; L_i , tube length; M, metallic axle; P, peristaltic pump; Q_i , flow rates; V_1 , volume of sample loop; V_2 , volume of lanthanum(III) loop; X, splitting point; Y, confluence; W, waste. Calcium determination: D, atomic absorption spectrophotometer; L_1 , 50 cm; L_2 , 70 cm; L_3 , 70 cm; Q_1 , 6.0 mL/min; Q_2 , 3.2 mL/min; Q_3 , 5.4 mL/min; V_1 , 95 μ L; V_2 , 120 μ L. Sodium and potassium determination: D, flame emission spectrometer; L_1 , 50 cm; L_2 , 20 cm; L_3 , 50 cm; Q_1 , 6.0 mL/min; Q_2 , 3.2 mL/min; Q_3 , 6.0 mL/min; V_1 , 95 μ L; V_2 , not used.

of the manifold parameters was carried out to meet the calcium determination requisites, and small modifications were established for the sodium and potassium determinations.

The sample was injected ($V_1 = 95 \mu\text{L}$) in the water carrier stream ($Q_1 = 6 \text{ mL/min}$), being the amount of analyte significantly reduced in the splitting point X by selecting a flow rate ratio Q_1/Q_2 of 1.9. The portion flowing to the detector was further dispersed along tube L_1 until confluence Y, where an additional dilution occurred. The plug was subsequently directed to the detector through L_3 . For the calcium determination, a lanthanum(III) solution was injected in valve V_2 . As the two valves are coupled, their switching occurs simultaneously, allowing the merging of both sample and lanthanum plugs in confluence Y by appropriate selection of L_2 length and Q_3 flow rate.

A 50 cm tube was chosen for L_1 , as shorter lengths did not provide reproducible results. The dispersion occurring along the 50 cm tube minimizes the effect of flow pulses from the peristaltic pump on the reproducibility of the splitting at point X. A longer tube would unnecessarily increase dispersion and decrease the sampling rate. Flow rate Q_3 was set to 5.4 mL/min to impose a flow rate 2 mL/min higher than the nebulizer aspiration rate, thus diminishing the analytical signal by reducing the nebulization efficiency. The joint effect of the overall dilution capacity of the manifold and the overpressure at the nebulizer entry allowed performance of determinations in the linear range corresponding to the usual concentration interval of calcium in beer. Using the preset parameters, the coil length L_2 was then studied to ensure that sample and lanthanum plugs arrive to the confluence point Y at the same time, which was achieved with a 70 cm tube. Besides their simultaneous merging, it was also necessary to guarantee the total inclusion of sample plug by the reagent zone; this was accomplished by injecting 120 μL (V_2) of lanthanum(III) solution.

There was no need for the addition of the releasing agent for sodium and potassium determinations, since no chemical interferences occur for these determinations by flame emission spectrometry. Therefore, no reagent was injected in the Q_3 water stream, and so the V_2 valve was not used. For these determinations, as a slightly

Table 1. Comparison of the Results Obtained by the Developed FIA Systems (C_f) and by the Reference Procedures (C_r); Relative Standard Deviations and Sampling Rates of the Developed FIA Systems

	values of the equation $C_f = C_0 + SC_r$			samples analyzed		characteristics of the FIA systems	
	C_0^a (ppm)	S^a	r^b	no.	concn range (ppm)	RSD ^c	sampling rate (h ⁻¹)
calcium	-0.2 (±0.4)	1.001 (±0.005)	0.9996	16	47.4–139	1.60 (67.3) 1.04 (101) 0.64 (124) 1.21 (93.9)	150
magnesium	1.3 (±1.5)	0.9878 (±0.014)	0.9967	15	61.2–155	0.64 (124) 0.73 (155) 1.30 (73.3)	120
sodium	-0.5 (±0.9)	1.005 (±0.011)	0.9980	16	50.5–125	0.96 (107) 0.85 (125) 1.10 (222)	150
potassium	-0.5 (±2.3)	1.004 (±0.007)	0.9991	17	222–462	0.60 (349) 0.32 (462)	200

^a The values in parentheses are the limits of the 98% confidence intervals. ^b Correlation coefficient. ^c Relative standard deviations (%) obtained from 10 consecutive injections of beer samples; concentrations (ppm) indicated in parentheses.

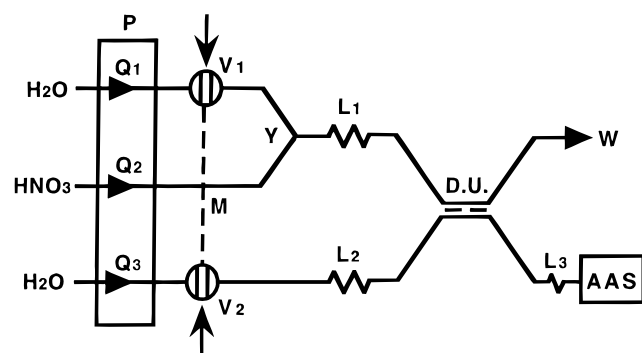


Figure 2. Flow injection manifold developed for the determination of magnesium in beer: AAS, atomic absorption spectrophotometer; D.U., dialysis unit; L_i , tube lengths ($L_1 = 50$ cm; $L_2 = 50$ cm; $L_3 = 20$ cm); M, metallic axle; P, peristaltic pump; Q_i , flow rates ($Q_1 = Q_2 = 2.5$ mL/min; $Q_3 = 5$ mL/min); V_1 , sample loop volume (200 μ L); V_2 , lanthanum loop volume (500 μ L); Y, confluence; W, waste.

higher dilution capacity was necessary, dilution in confluence Y was extended by increasing the flow rate Q_3 up to 6 mL/min. Therefore, the analytical signal was reduced not only because of the increased dilution factor in this confluence but also because of augmented overpressure at the entry of the nebulizer.

The sampling rates achieved with this setup were of ~ 150 samples/h for calcium and sodium determinations, and 200 samples/h for potassium determination.

Determination of Magnesium. As the amounts of magnesium in beer are much higher (80–320-fold) than the working linear concentration range for this determination using atomic absorption spectrometry, the above mentioned manifold did not yield sufficient dilution capacity. In order to reach these dilution requirements with a relatively simple FIA system, a dialysis unit was incorporated (Figure 2).

The dialysis unit in the FIA system separates two streams, the donor containing the sample plug and the acceptor leading the dialysate to the detector. Due to the low efficiency of the membrane diffusion process, large dilutions are easily obtained because there is a substantial reduction in the amount of analyte flowing to the detector. In this manifold, sample or standards and lanthanum(III) solution were simultaneously injected in the system by means of the two coupled injection valves (valves V_1 and V_2 , respectively). The parameters of the system, namely, flow rates Q_1 , Q_2 , and Q_3 and coil lengths L_1 and L_2 , were set to ensure that the two plugs flow through the dialysis unit at the

same time, being the dialysate received by the lanthanum solution plug, and taken to the detection system by L_3 .

The manifold also included a confluence point (Y) where a 0.3 M HNO_3 solution was added to samples and standards. The inclusion of this confluence point in the system became necessary because the pH of the injected solutions affects the diffusion process (Ferreira et al., 1995). The addition of 0.3 M HNO_3 to samples and standards made the dialysis process independent of the different composition of samples and standards, namely, in terms of pH, since it was possible to ensure a constant H^+ concentration along the sample and reagent plugs before reaching the dialysis membrane.

The flow rate Q_3 was adjusted to the normal uptake rate of the atomic absorption nebulizer (5 mL/min). The flow rates Q_1 and Q_2 were both set at 2.5 mL/min, so that equal flow rates for the donor and acceptor streams could be obtained.

The length of coil L_1 was selected as the minimum length that provided a good mixing of the merging solutions after the confluence point, in order to obtain reproducible results. The length of reactor L_2 was selected as the one that made both sample and lanthanum plugs coincident when passing through the dialysis unit using the preset flow rates.

Sample loop volume (V_1) was set to 200 μ L. A volume of 500 μ L was used for the lanthanum(III) loop (V_2), yielding peak heights similar to those obtained when the lanthanum(III) solution was used as Q_3 carrier stream (instead of injecting the same solution in a water carrier stream).

By using this manifold, a sampling rate of ~ 120 samples/h was achieved.

Analysis of Beer Samples. The beer samples were injected in the flow injection manifolds, and the cation concentrations calculated by interpolation in the previously established calibration plots (Figure 3); the calculations were based on peak height.

In order to assess the quality of the FIA results, analyses of beer samples, using the flow injection manifolds and the manual methods for the same detection systems, were carried out; between the respective results C_f and C_r , a relation of type $C_f = C_0 + SC_r$ was established for each cation determination, this being the equation parameters as well as the 98% confidence limits (Miller and Miller, 1993) presented in Table 1.

From these figures it is clear that there is no evidence for systematic differences between the results obtained by the two methodologies, as slopes and intercepts do

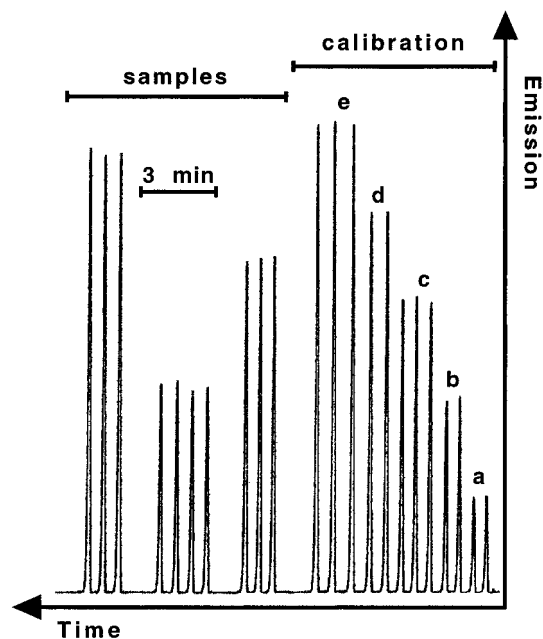


Figure 3. FIA register obtained for the determination of potassium in beer corresponding to injections of standards [(a) 100, (b) 200, (c) 300, (d) 400, and (e) 500 ppm] and samples.

not differ significantly from unity and zero, respectively. The maximum relative deviations observed between the two methodologies, calculated as $[(C_f - C_r)/C_r] \times 100$, were 3.6% for sodium, 2.4% for potassium, 2.3% for calcium, and 3.8% for magnesium.

To assess the reproducibility of the FIA procedure, the relative standard deviations were calculated for 10 consecutive determinations of three beer samples with concentrations covering the analytical range for each analyte. The reproducibility was good, the relative standard deviations observed being lower than 1.6% for 10 consecutive measurements (Table 1).

Conclusions. The developed FIA systems are advantageous alternatives to the conventional procedures for determination of cations in beer samples as they permit automatic beer sample preparation for instrumental measurement with high sampling rates and they achieve quality results with good reproducibility. Lanthanum(III) consumption is reduced in the automatic determinations compared with the consumption when conventional methodologies are used.

An additional advantage is the possibility of performing bicomponent analysis on the same injected sample. In fact, in the manifold for calcium, sodium, and potassium determinations, there is a sample portion that is wasted after the flow splitting that could be of analytical use. The solution in this channel could be submitted to an appropriate treatment and led to another detector and so another species could be deter-

mined. As for the FIA system for magnesium determination, a bicomponent analysis in the same injected sample plug is also feasible. Because the sample plug in the dialysis unit becomes divided in two separate streams, both sample boluses can be directed to different detectors.

Finally, it should be stressed that the cost of implementing these FIA systems in a quality control laboratory is quite low when compared to the cost of the atomic spectrometers. Consequently, the acquisition of such equipment might represent a good investment if one considers the many advantages taken from it and the low cost of its implementation.

ACKNOWLEDGMENT

We are thankful for collaboration with the brewery UNICER—União Cervejeira, SA, Leça do Balio, Portugal.

LITERATURE CITED

- Bengamin, F^o; Zagatto, E.; Krug, F.; Reis, B. Merging zones in flow injection analysis. Part I. Double proportional injector and reagent consumption. *Anal. Chim. Acta* **1978**, *101*, 17–23.
- Buckee, G. K. Anions and cations. *Ferment* **1991**, *4*, 38–39.
- Charalambous, G.; Bruckner, K. J. Analysis of metallic ions in brewing materials, wort, beer and wine by inductively coupled argon plasma—atomic emission spectroscopy. *Tech. Q. Master Brew. Assoc. Am.* **1977**, *14*, 197–208.
- Fernandes, S. M. V.; Lima, J. L. F. C.; Rangel, A. O. S. S. Colorimetric determination of iron in beer by flow injection analysis using the merging zones technique. *J. Inst. Brew.* **1995**, *101*, 281–284.
- Ferreira, A. M. R.; Lima, J. L. F. C.; Rangel, A. O. S. S. Flow injection simultaneous determination of basic cations pairs in soils. *Soil Sci.* **1995**, *159*, 331–336.
- Hough, J. S.; Briggs, D. E.; Stevens, R.; Young, T. W. Chemical and physical properties of beer. In *Malting and Brewing Science*; Chapman and Hall: London, England, 1982.
- Lima, J. L. F. C.; Neves, O. B. A. O.; Rangel, A. O. S. S. Flow injection determination of reducing sugar in wine in a wide concentration range using a dialysis unit and a stream splitting. In *Automatic Control of Food and Biological Processes*; Bimbenet, J. J., Dumoulin, E., Trystram, G., Eds.; Elsevier Science: Amsterdam, Holland, 1994.
- Miller, J. C.; Miller, J. N. Errors in instrumental analysis; regression and correlation. *Statistics for Analytical Chemistry*; Ellis Horwood: Chichester, England, 1993.

Received for review June 18, 1996. Accepted January 2, 1997. © S.M.V.F. gratefully acknowledge support from PRAXIS XXI (Grant BD/2851/93-IF). Support from PAMAF/IDARN project 24 is also acknowledged.

JF9604347

© Abstract published in *Advance ACS Abstracts*, February 15, 1997.