

## Multicomponent Flow Injection Analysis: Determination of Potassium and Calcium in Wine

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### ABSTRACT

*A flow injection potentiometric method for simultaneous determination of potassium and calcium is suggested. The optimized double-channel flow system, in relation to component, speed of carrier solution, volume of the sample and length of the mixing tube, is characterized with high productivity (30–60 samples per hour) and simple technical equipment.*

*The method is applied for analysis of wine. In this case, the reproducibility of results is lower than 2% while the accuracy, as compared with other methods, is not more than 5%.*

*No preliminary treatment of the wine sample is required.*

### INTRODUCTION

Flow injection analysis is the most effective method for automation of the chemical analysis of liquid samples. Its use proved to be of special importance in laboratories performing serial analyses (Ligue de Castro & Valcarcel, 1984; Trojanowicz, 1984), such as analyses in which it is necessary to determine several components in a great number of samples. The properties of wine are determined, to a great extent, by the content of potassium and calcium. Their content is usually 400–800 mg/litre for potassium and 30–100 mg/litre for calcium.

Various methods have been suggested in the literature for determination of potassium and calcium in wines: classical, electrochemical, radiochemical and spectroscopic (Baluja-Santos *et al.*, 1984; Da-Ren *et al.*, 1985; Goranov

*et al.*, 1986). Some authors recommend the atomic absorption method for determination of potassium, and flame photometry for calcium (Junge, 1987). Determinations have also been communicated in the literature with the help of calcium and potassium ion-selective electrodes (ISE) (Casanova, 1974; *Methods Manual*, 1979). All the above mentioned methods require preliminary treatment of the samples and repeated dilution of most of them.

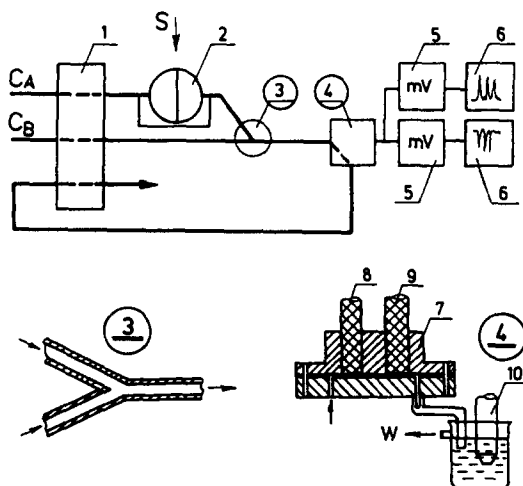
There are no data in the literature about simultaneous determination of potassium and calcium with the help of flow injection potentiometry (FIP-SD).

The purpose of this work is to develop and apply FIP for simultaneous determination of potassium and calcium in wines.

## MATERIALS AND METHODS

### Flow injection system

Use is made of a two-channel flow injection system (Fig. 1) with serial indicator electrodes and a common reference one. The flow carrier  $C_A$  (in all cases—bidistilled water) and ionic strength/pH adjustment buffer  $C_B$  (ISA) are removed at an equal velocity by a peristaltic pump (ISMATEC). The samples are injected with a two-position home-made injector with two identical sample loops. The EMFs of the electrochemical cells are measured at room temperature, using two mV-meters (OP-208, Radelkis), each connected with the device for signal recording (Polarograph OH-205,



**Fig. 1.** Schematic diagram of the flow injection system. 1, peristaltic pump; 2, injection valve; 3, Y-connector; 4, detector cell; 5, pH/mV-meter; 6, recorder; 7, teflon body of the detector cell; 8, calcium selective electrode; 9, potassium selective electrode; 10, reference electrode;  $C_A$ , carrier solution ( $H_2O$ );  $C_B$ , ionic strength/pH adjustment buffer; W, waste.

Radelkis). The detector cell is made out of teflon, the distance between the electrodes being 7 mm. The two indicator electrodes are made by Radiometer, while the reference one—saturated calomel electrode—is by Radelkis. Teflon tubes are used with inner diameter 0.7 mm.

### Reagents

All chemicals (KCl, CaCl<sub>2</sub>, CH<sub>3</sub>COONa, NaCl) are analytical grade and use is always made of bidistilled water. The working solutions were prepared every day. All solutions are degasified before work, using a water vacuum pump.

### Buffer system

NaCl and CH<sub>3</sub>COONa are studied from 0.1 to 0.2M.

### Calibration of the electrodes

The calibration curves are obtained by injecting mixtures of KCl and CaCl<sub>2</sub> solutions (from 0.05 mM to 2.0 mM for K<sup>+</sup> and Ca<sup>2+</sup>). A fixed volume of the calibrating solution (50–100 μl) is injected in the flow of bidistilled water, then it is mixed with the flow from ISA (Fig. 1). The signals obtained, proportional to the content of K<sup>+</sup> and Ca<sup>2+</sup>, are treated by the method of regression analysis.

### Procedure for determining K<sup>+</sup> and Ca<sup>2+</sup> in wine

The electrodes are calibrated by injecting mixed standard solutions of K<sup>+</sup> and Ca<sup>2+</sup> in the concentration range 100–1000 mg/litre and 10–100 mg/litre, respectively (see Table 3). The wine samples (50–100 μl) are injected without any preliminary preparation. Some 0.1M CH<sub>3</sub>COONa is used as ISA.

## RESULTS AND DISCUSSION

### Optimization of the system

As compared to the one-channel, the two-channel flow injection system provides a number of advantages: eventual differences in ionic strength, pH, temperature and viscosity between the calibration solutions and those of the samples are eliminated. Preliminary treatment of the samples is thus avoided.

The parameters of the system were altered as shown in Table 1, with a view to achieving a maximal linear part of the calibration curves, speed of

**TABLE 1**  
Optimization of the Flow Injection System

<i>Parameter</i>	<i>Dimension</i>	<i>Interval of change or reagent change</i>	<i>Optimum</i>
Speed of carrier solution— $C_A$	ml/min	1–2	1
Speed of ISA, $C_B$	ml/min	1–2	1
Component of $C_A$	—	—	H <sub>2</sub> O
Component of $C_B$	—	NaCl CH <sub>3</sub> COONa	CH <sub>3</sub> COONa
Ionic strength, $C_B$	M	0.1–0.2	0.1
Volume of sample	μl	50–100	100
Mixing coil length with 0.7 mm i.d.	cm	10–50	25

analysis, accuracy and stability of the base line. Particularly important proved to be mixing chamber dimensions. A compromise should be made between good homogenization of both flows and the achievement of low sample dispersion. Good homogenization is attained by increasing the length of the mixing chamber. However, in this case the dispersion of the sample also grows. In our system, a mixing chamber with inner diameter of 0.7 mm and length of 25 cm provided both stability of the base line and high sensitivity for the two components (Table 1).

### Characteristics of the optimized system

Table 2 shows the final characteristics of the system (4th column of Table 1). As the table makes clear, the rate of analysis may be doubled by adding

**TABLE 2**  
Results of the Optimized Flow Injection System for Simultaneous Determination of Potassium and Calcium

Nerstian range (mM):	0.05–2
for Ca <sup>2+</sup>	0.05–2
for K <sup>+</sup>	
Dispersion <sup>a</sup> (log D):	
for Ca <sup>2+</sup>	0.60
for K <sup>+</sup>	0.65
Sampling rate (h <sup>-1</sup> )	30
If to the carrier streams are added 2.5 mg/litre K <sup>+</sup> and 25 mg/litre Ca <sup>2+</sup> the sampling rate is	60

<sup>a</sup> Calculated in accordance with Trojanowicz (1984).

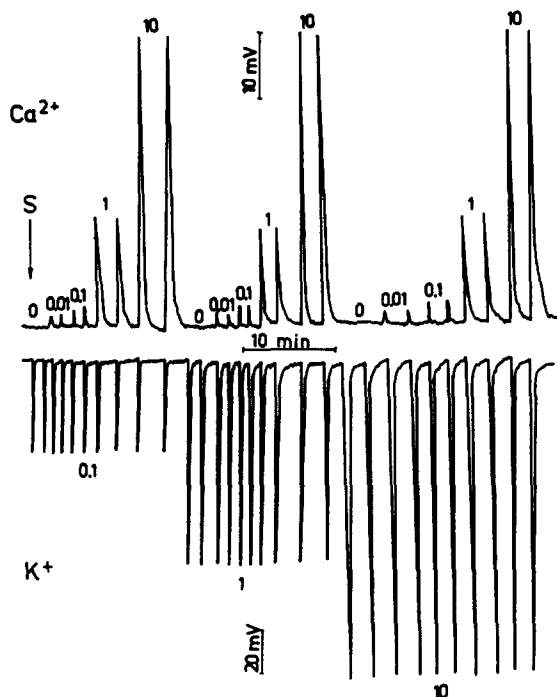


Fig. 2. Analytical signals from mixed solutions ( $K^+$  and  $Ca^{2+}$ ). The concentration of the components in mM is shown in the figure with numbers. Flow rate for each of the carrier solutions = 1.0 ml/min. Volume injected = 100  $\mu$ l.

small amounts of the potentially determining ions in the flow carrier (Ilcheva *et al.*, 1987; Trojanowicz & Frenzel, 1987). Figure 2 demonstrates the possibility of simultaneous determination of  $K^+$  and  $Ca^{2+}$ . As the figure illustrates, the presence of potassium ions exerts no influence on the signal of the calcium electrode, and *vice versa*—the calcium ions exert no

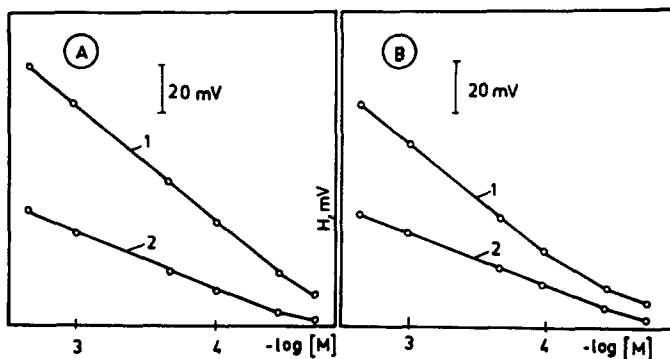


Fig. 3. Calibration curves: 1,  $K^+$ ; 2,  $Ca^{2+}$ . (A) Ionic strength adjustment—0.1M  $CH_3COONa$ . (B) Ionic strength adjustment—0.1 M  $NaCl$ . Flow rate for each of the carrier solutions = 1.0 ml/min. Volume of injected solution = 100  $\mu$ l.

**TABLE 3**  
Calibration Solution Design for Simultaneous Determination  
of Potassium and Calcium in Wine

<i>Mixture</i>	<i>Ca<sup>2+</sup> (mg/litre)</i>	<i>K<sup>+</sup> (mg/litre)</i>
1	10	100
2	20	200
3	40	400
4	60	600
5	80	800
6	100	1 000

**TABLE 4**  
Characteristics of Calibration Plots Obtained for Ca<sup>2+</sup> and K<sup>+</sup> Selective  
Electrode in FIP-SD

<i>Electrode</i>	<i>Volume of sample (ml)</i>	<i>H<sup>0</sup> (mV intercept)</i>	<i>Slope (mV/dek)</i>	<i>r (coefficient of correlation)</i>
K <sup>+</sup>	50	202.7	57.2	0.999 1
	75	232.3	57.0	0.999 3
	100	246.4	57.9	0.999 2
Ca <sup>2+</sup>	50	105.7	20.9	0.998 2
	75	120.1	26.9	0.998 9
	100	136.5	27.9	0.999 2

**TABLE 5**  
Reproducibility of the Results of Simultaneous Determination of  
Potassium and Calcium in Wine

<i>Component</i>	<i>Volume of sample (μl)</i>	<i>Found (mg/litre)</i>	<i>Number of determinations</i>	<i>Relative standard deviation</i>
K <sup>+</sup>	50	660	6	0.02
Ca <sup>2+</sup>		43.9	6	
K <sup>+</sup>	75	665	5	0.02
Ca <sup>2+</sup>		45.1	5	
K <sup>+</sup>	100	660	5	0.01
Ca <sup>2+</sup>		45.7	5	

**TABLE 6**  
Results from FIP-SD for  $K^+$  and  $Ca^{2+}$  in Wine Samples

Sample wine	$K^+$ (mg/litre)			$Ca^{2+}$ (mg/litre)		
	FIP-SD present work	Conventional potentiometry	Deviation (%)	FIP-SD present work	Titrimetric method	Deviation (%)
1	570	565	+0.3	41.70	42.2	-1.2
2	555	560	-0.9	36.9	37.2	-0.8
3	435	440	-1.1	35.1	33.8	+3.8
4	465	465	0	33.9	34.9	-2.9
5	660	655	+0.8	45.7	44.3	+3.2

influence on the signal of the potassium electrode. The effect of ISA on the electrode functions is not essential. Some 0.1M  $CH_3COONa$  was used since, in this case, the signals for potassium are more intensive (Fig. 3, curve 1). Besides, in this case, an optimum pH value for  $Ca^{2+}$ -ISE is also maintained (Midgley & Torrance, 1980).

### Application

The optimized flow injection system was applied to determination of  $K^+$  and  $Ca^{2+}$  in wines. The calibration curves, evaluating the expected contents of  $K^+$  and  $Ca^{2+}$ , are obtained with mixed solutions, the compositions of which are indicated in Table 3. Under these conditions, the functions of the electrodes are linear, with  $r \geq 0.9982$  (Table 4). Table 5 shows the reproducibility of the results from FIP-SD of  $K^+$  and  $Ca^{2+}$  for one sample with different injection volumes—50, 75 and 100  $\mu$ l. A systematic error is not observed and the reproducibility is 1–2%.

The data in Table 6 show the results from analysis of five wine samples (each is a mean value of six measurements). The results of FIP are compared with those of conventional potentiometry for  $K^+$  (*Methods Manual*, Orion, 1979) and a titrimetric method for  $Ca^{2+}$  (Casanova, 1974), and the deviation is from 0 to 4% (Table 6).

### CONCLUSION

The suggested flow injection potentiometric method for simultaneous determination of potassium and calcium is characterized with high productivity (30–60 samples per hour) and simple technical equipment.

The method is applied for determining the two components in wine. In

this case, the reproducibility of the results is lower than 2%, while the accuracy as compared to other methods is not more than 4%.

No preliminary treatment of the wine samples is required.

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