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# A Variable Volume Injector Applied to the Atomic Absorption Determination of Sodium, Potassium, Calcium and Magnesium in Blood Serum by Flow Injection Analysis

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SUMMARY

Samples can be reproducibly introduced into a flow system by means of a variable volume injector. This injector has been used to the atomic absorption determination of sodium, potassium, calcium and magnesium in blood serum with a good accuracy by injecting various volumes of a single standard solution into a flowing system.

## INTRODUCTION

The curvature of calibrations in atomic absorption spectrophotometry (AAS) has been recognised since its conception in 1955 (1). Flame atomic absorption instruments, in particular, do not give a linear response with increasing analyte concentration, owing to a variety of effects such as nebulisation, atomisation and measurement processes. It has been shown that an acceptable analytical performance may be obtained by fitting curves to the calibration data when working in regions where the calibrations are strongly curved

(2). Manual and microcomputer-linked instruments have been used for fitting curves to the calibration data, however, as the equation (or various equations) for the calibration function is empirical, errors will always occur. Errors due to the curve fitting procedure will only be overcome if alternative methods of calibration are employed. A simple variable volume injector for flow injection analysis (3) has been recently used to bring sample concentration on-range by injecting different volumes of a known analyte content. In this way, the construction of a calibration graph from a single standard solution was possible. In this paper variable volumes of a single standard solution containing sodium, potassium, calcium and magnesium as well as other chemical species at typical blood serum physiological concentrations has been used in order to determine unknown electrolyte concentrations in blood serum samples. Therefore, here the use of the variable volume injector in routine analysis and in the development of new procedures is demonstrated.

## EXPERIMENTAL

### Reagents, Standards and Samples

All reagents were of analytical grade, unless otherwise stated, and all water was distilled and deionized. For the chemical species determination a stock solution of 10000 mg $l^{-1}$ of sodium and 1000 mg $l^{-1}$ of potassium, calcium or magnesium were prepared. Working solutions were prepared daily by appropriate dilution with a solution containing physiological amounts of the other chemical species (4). Each stock and working solution contained 50 and 80 g $l^{-1}$ glycerol and EDTA, respectively.

The glycerol was added to adjust viscosity and EDTA was added to match more closely ionic conditions present in serum (4). Blood serum samples were collected, treated and handled as previously described by Burguera et al. (5).

## Apparatus and Manifold

The instrumental used here was as reported by Burguera et al. (6). The flow injection system is based on Burguera et al. manifold (3) illustrated in Fig. 1, labelled according to their conventions.

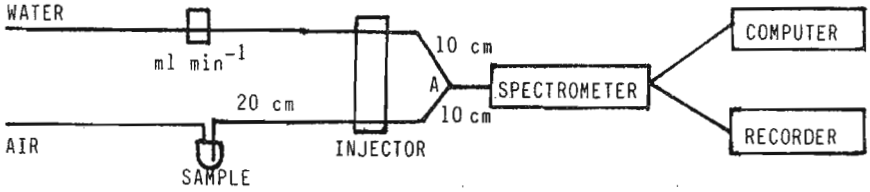


Fig. 1 Flow diagram for the determination of sodium, potassium, calcium and magnesium using the variable volume injector

The variable volume injector is a time controlled device of a continuously moving rotor (R) in contact with a six axially drilled holes isolated flat metal plate (MP) made of stainless steel (Fig. 2). A switch (S) connects R with a given section of MP, and in this way repetitive pulses are dispensed to the solenoide (SL) (Fig. 2 and 3).

## PROCEDURE

The optimum operating conditions are summarized in Table 1. As the coil current of SL is turned on and off at a fixed interval, it initiates a sequence which leaves the solenoid inactive for 4.5, 4.0, 3.5, 3.0, 2.5 and 2.0 s followed by

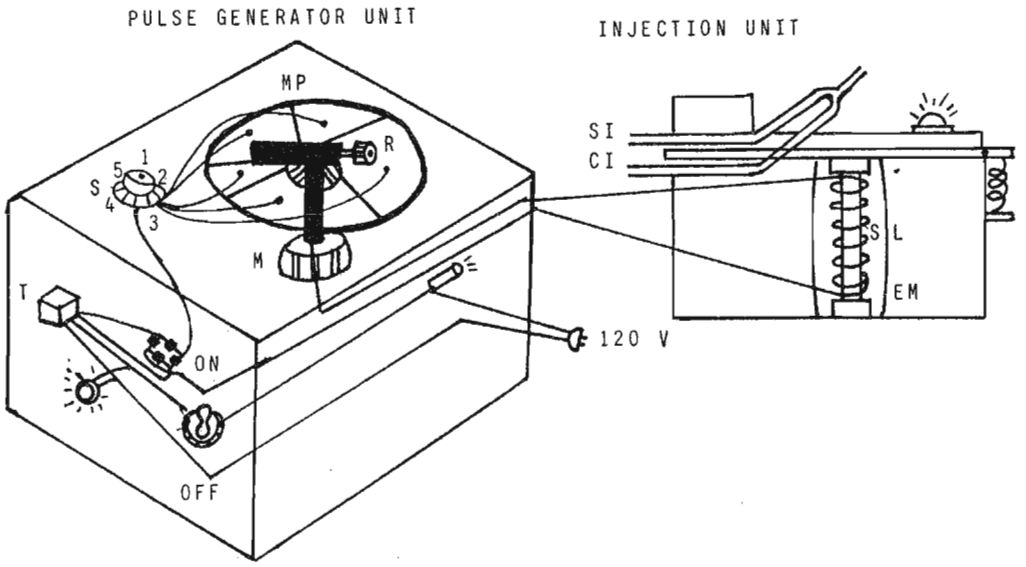


Fig. 2 Schematic drawing of the pulse generation and injection units. T, transformer; S, switch; MP, metal plate; R, rotor; M, rotor motor unit; SI, sample introduction; CI, carrier stream; SL, solenoid; EM, electromagnet

activation of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 s, respectively. The inactive periods occur when R is in contact with the unconnected section of MP. The sequence of the injection of a given sample or standard is carried on without resetting. In this way 4, 14, 22, 34, 48 or 62 µl are injected with a precision of 0.3-0.6 % relative standard deviation, which comfirms the high degree of precision of each volume injected and therefore the reliability of this injection approach (3). The very high sampling rate obtained (ca. 400 measurements per hour) was higher or at least just as high as in most flow injection systems previously described.

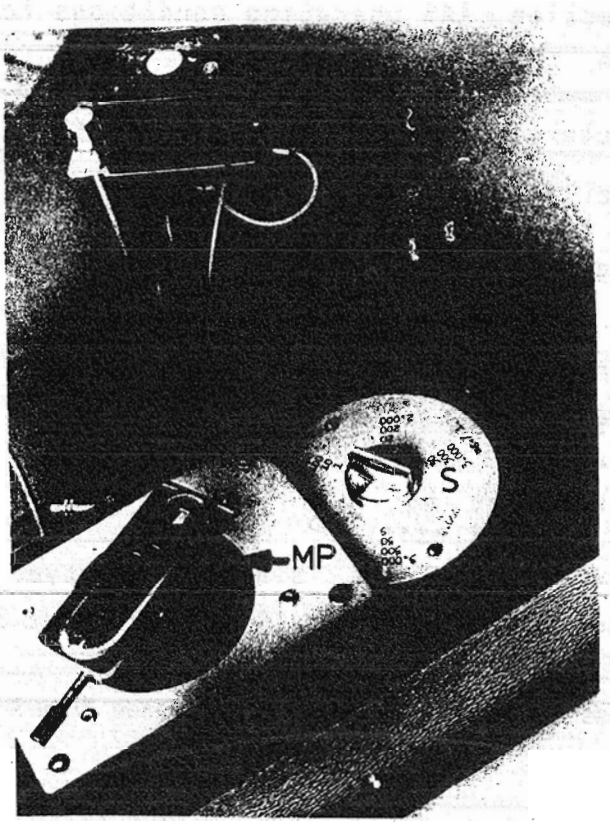


Fig. 3 Pulse generation and injection units of the variable volume injector

## RESULTS AND DISCUSSION

### Variation in Sensitivity for Different Volumes

Fig. 4 depicts the calibration curves for the determination of sodium, potassium, calcium and magnesium by injecting different sample volumes. At higher volumes, using the same concentration of solutions, the sensitivity of measurements increased but, at the same time, calibration graphs become non-linear, excepting calcium in the range 40 to 120 mg $l^{-1}$.

TABLE 1 Flow injection - AAS operating conditions for sodium, potassium, calcium and magnesium*

| Component | Parameters | Na | K | Ca | Mg |
|---|---|---|---|---|---|
| Flow injection | Carrier flow rate, ml $min^{-1}$ | 3.5 | 3.5 | 2.5 | 2.5 |
| | Tubing length**, cm | 100 | 100 | 55 | 120 |
| AAS | Lamp current, mV | 5.0 | 5.0 | 3.5 | 4.0 |
| | Wavelength, nm | 330.3 | 766.5 | 422.3 | 285.2 |
| | Slit-width, l $min^{-1}$ | 0.5 | 1.0 | 0.5 | 1.0 |
| | Burner height, mm below optical axis | 15 | 15 | 10 | 11 |
| | Burner | Single slot type | | | |
| | Air\|acetylene, l $min^{-1}$ | 9.5/1.5 | 9.5/1.5 | 16.5/2.3 | 16.5/2.3 |

*The sample volume was variable (see text), **distance from A to the detector (Fig. 1).

However, by preparing standards that give absorbances within the linear range, i.e. 3000, 150, 80 and 24 mg $l^{-1}$ of sodium, potassium, calcium and magnesium, respectively, calibration graphs from a single solution are obtained by injecting incremental volumes of known samples (Fig. 4, a-c)

Precision and Accuracy

The precision of eight replicate analysis: 1.5 ± 0.5, 1.2 ± 0.4, 0.8 ± 0.4 and 1.2 ± 0.5 % RSD (relative standard deviation) for the determination of 75, 4, 2 and 0.5 µg of sodium, potassium, calcium and magnesium, respectively, is satisfactory considering the low concentration of each

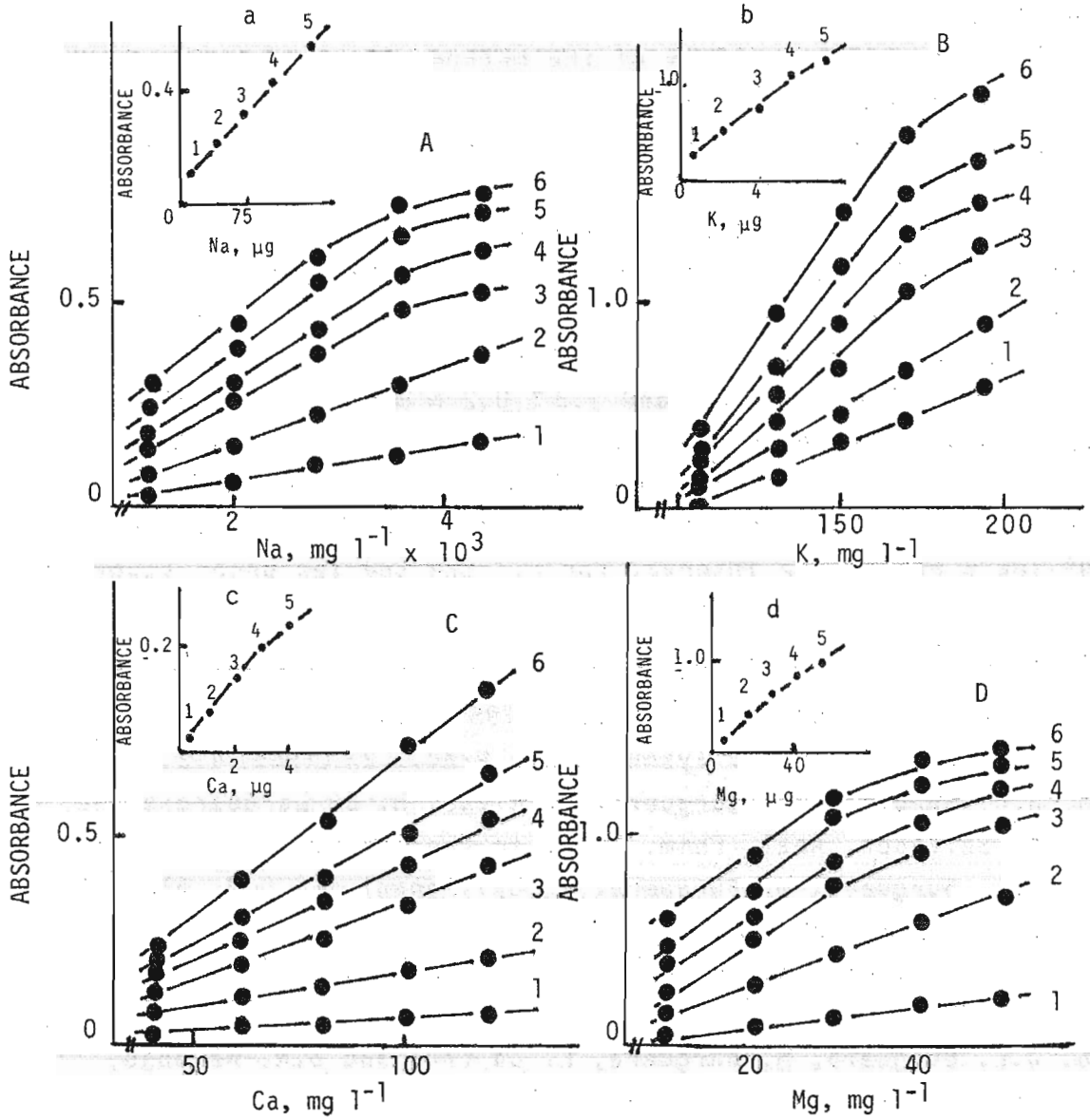


Fig. 4 A-D: Variation in peak heigth with sample volume. 1 to 6 indicate the sample volumes 4, 14, 22, 34, 48 and 62 µl, respectively.

a-d: Calibration graphs for sodium, potassium, calcium and magnesium from a single solution of absorbance vs. analyte amount by injecting incremental known sample volumes. 1 to 5 indicate sample volumes 4, 14, 22, 34 and 48 µl, respectively.

metal specie.

To check the accuracy of the method, 22 μl of human serum with known content of the elements (4,7) were analyzed. Results were in good agreement (within the 96-101 % confidence limit) with those previously obtained (4,7). Accuracy was further tested by analyzing the National Bureau of Standards Standard Reference Material (NBS SRM) No. 909, Freeze-Dried Serum. The mean (± SD) concentrations of sodium, potassium, calcium and magnesium in this reference material were 155.8 ± 2.5, 4.3 ± 0.2, 3.4 ± 0.1 and 1.3 ± 0.2 m mol $l^{-1}$ $g^{-1}$, while the proposed concentrations were 158.4 ± 1.0, 4.155 ± 0.011 , 3. 560 ± 0.004 and 1.425 ± 0.015 m mol $l^{-1}$ $g^{-1}$, respectively. As a result, the values here reported are well the uncertainty 95-104 % confidence interval for all the species under study.

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