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Simultaneous determination of lithium, sodium and potassium in blood serum by flame photometric flow-injection analysis

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Abstract

A simultaneous flow-injection analysis (FIA) manifold that could analyse three ions from a single injection was designed, constructed, calibrated and used successfully to analyse Li^+, Na^+ and K^+. This FIA method was 10 times faster than the batch technique. The sample volume required was a fraction of about 1/110 to 1/75 that of the batch technique. The outputs were quite reproducible and calibration curves were linear. Results obtained for artificial sera compared favourably with the actual known concentrations of ions and results obtained in the analysis of eight natural human blood sera compared well with those obtained by the traditional batch technique.

Keywords: Flow-injection analysis; Blood serum; Lithium; Sodium; Potassium

1. Introduction

Blood electrolytes are cations and anions present in sera which perform various functions [1] for human health. Regular monitoring of these ions is important because deficiency or excess of these ions can cause serious health defects. The routine determination of these ions is by separate batch techniques [2–4] where fresh blood serum is taken to determine each ion, i.e. one sample for every ion analysis. This is time-consuming, wasteful in terms of blood serum and labour-intensive. In this paper, the description of the design, construction and use of a flow-injection analysis (FIA) manifold [5–7], involving sample zone splitting [8,9], which could analyse three blood ions simultaneously from just one sample injection, is given. The process involves the splitting of the injected sample zone into three different coils of different coil lengths, the three sample portions reach the detector at different times and are used to determine the ions in turn by moving the filter on the detector from one ion to another.

2. Experimental

2.1. Apparatus and manifold construction

The manifold designed to serve the purpose of one sample–three ion analysis is shown in Fig. 1.

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An air compressor system was used to force distilled water (carrier stream) out of an enclosed container to flow through the tubings. The tubings were made of PVC and had an internal diameter (i.d.) of 1.0 mm. An injection valve, equipped with a simple syringe, was used to introduce the sample, reproducibly, into the carrier stream. A splitting system split the sample zone at point S into three separate coils C_1, C_2 and C_3. Due to the different coil lengths, the sample portions reach the detector at different times and are used to determine the different ions in turn.

The splitting system, constructed on a perspex plate, is shown in Fig. 2. S, E, 1, 2 and 3 are smooth holes of 0.25 cm depth and 2.00 mm i.d. drilled on a perspex plate of 0.5 cm thickness. These holes sit on smaller holes of 0.25 cm depth and 1.0 mm i.d on the underside of the plate. On the underside of the plate, S is connected to the adjacent holes 1, 2 and 3 by smooth route paths of 1.0 mm i.d. The underside of the plate is sealed completely with PVC tape without blocking the holes and route paths. PVC tubings of 0.7 cm length and 1.0 mm i.d. were fixed into the larger holes on the upperside of the plate with a glue prepared by dissolving perspex powder in a 50:50 mixture of $CHCl_3$ and THF. The holes 1, 2 and 3 on one side are connected to 1, 2 and 3 respectively on the other side by PVC tube coils C_1, C_2 and C_3 respectively. Point E is a point of confluence which all sample portions pass before reaching the detector. Thus it was possible to determine one ion from one sample portion and then to turn the filter to another ion to be determined from the next sample portion. The detector used was the single window PFP 7 flame photometer manufactured by Jenway Ltd., UK. The Endim 621-02 recorder, produced by the "Neptum" Schlothin Company in Germany, was used in conjunction with the detector.

2.2. Reagents

Li^+, Na^+, and K^+ standard stock solutions, used to prepare calibration curves, were provided by Jenway Ltd. The concentrations of the standard stock solutions used were Li^+, 1.0 mmol l^{-1}; Na^+, 140.0 mmol l^{-1}, and K^+, 5.00 mmol

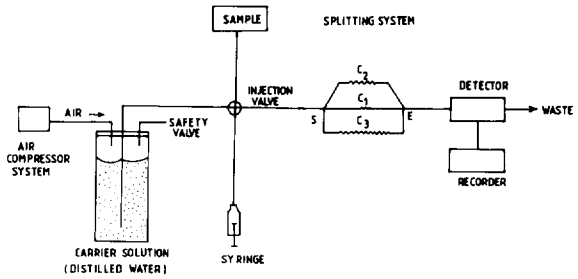

Fig. 1. Manifold design for one sample–three ion analysis.

l^{-1}. Doubly-distilled water was used as the blank/carrier solution. LiCl, NaCl, NaH_2PO_4, KCl and $MgSO_4 \cdot H_2O$ used for preparation of artificial blood sera were of reagent grade and were products of BDH (UK).

2.3. Calibration of analytical system (Optimum flow conditions)

The relative coil lengths C_1, C_2 and C_3 were optimised by successive injections of a 14.0 mmol l^{-1} Na^+ standard solution and adjustment of the lengths until the sample portions did not merge at the point of exit, E. The differences between the times when the sample portions reached the detector were sufficient to change the filter position from one ion to another and for a stable baseline to be obtained.

The respective dispersions D_1, D_2 and D_3 in the coils were determined by first aspirating directly a 14.0 mmol l^{-1} Na^+ standard solution and recording the detector output, then injecting this solution using doubly-distilled water as the carrier stream and recording the output from the coils,

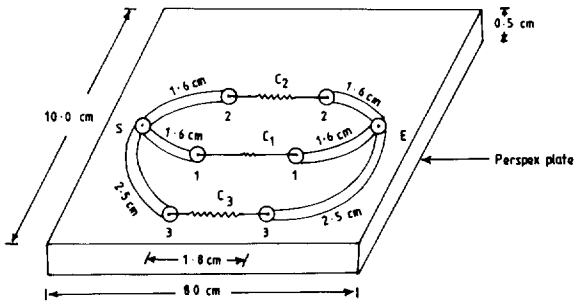

Fig. 2. Diagram showing construction of splitting system.

and then calculating the dispersion, D, from the formula

$$D = \frac{\text{output of direct pumping}}{\text{output of coil after injection}} \quad (1)$$

Each coil had its own residence time [7] which was measured with a stop-clock, as the time from injection to output maximum.

Optimum sample volume range was obtained by injecting various sample volumes of a 14.0 mmol l^{-1} Na^+ standard solution, recording the output, determining the corresponding dispersions in coils and the various differences between the times when the sample portions reached the detector, choosing the optimum sample volume range as that which gave good dispersions in coils for reliable output and optimum time separations for changing filter positions, zeroing the instrument, and having good resolution of peaks.

The optimum flow rate [7] was also determined after varying only the flow rate on subsequent injections of the 14.0 mmol l^{-1} Na^+ standard solution until a good output, time separations for changing filter positions, zeroing of the instrument and good resolution of peaks were obtained. To measure the sampling rate [7], the time from injection to detection of the third ion was noted and the sampling rate was calculated as the number of ions analysed per hour. Different concentration levels of the standard stock solution were then prepared and aspirated directly to obtain batch calibration plots [10,11] and these were then injected to obtain FIA calibrations plots for Li^+, Na^+ and K^+.

2.4. Preparation of standard solutions

The required volumes of the standard stock solution were taken and diluted to different levels to obtain concentration ranges of 0.01–1.0 mmol l^{-1} for Li^+; 14.0–140.0 mmol l^{-1} for Na^+; and 0.5–5.00 mmol l^{-1} for K^+ which were used for calibration curves for Li^+, Na^+ and K^+ respectively.

2.5. Pretreatment of natural blood serum samples

Eight blood serum samples were obtained from the Cape Coast central hospital. The serum samples were diluted ten-fold by adding 1 ml of 1.0 mmol l^{-1} Li^+ and 8 ml of doubly-distilled water to 1 ml of blood serum sample. The lithium was added to enhance the sensitivity of the flame photometer for Li^+ since the concentration of lithium in natural blood serum is very low (0.001 mmol l^{-1}).

2.6. Preparation of artificial serum

An artificial blood serum was prepared by taking 4.24×10^{-2} g of LiCl, 8.0716 g of NaCl, 0.1304 g of NaH_2PO_4, 0.381 g of KCl, 0.2792 g of $CaCl_2$ and 0.1408 g of $MgSO_4 \cdot H_2O$, dissolving in doubly-distilled water and diluting the mixture to the 1 l mark [12]. This gave concentrations of Li^+, 1.000 mmol l^{-1}; K^+, 5.113 mmol l^{-1}; and Na^+, 146.3 mmol l^{-1}. Similar preparations of other solution mixtures was done to obtain four other solutions with concentrations as follows:

Li^+ (mM)	K^+ (mM)	Na^+ (mM)
0.500	3.00	138.0
0.700	3.50	140.0
0.800	4.00	142.0
0.900	4.50	144.0

These five solutions were used for the analysis.

2.7. Analysis of blood serum samples

2.7.1. Batch process

The various standard solutions were first aspirated directly into the flame photometer and the results were used to obtain batch calibration plots for Li^+, K^+ and Na^+. The volume aspirated in each case was 3.0×10^3 μl, giving a total of 9.0×10^3 μl for the three ions. The eight different natural sera were aspirated directly and the concentrations of the ions were determined.

2.7.2. FIA process

100 μl portions of the standard solutions were injected into the carrier stream and the readings obtained were used to plot calibration curves for Li^+, K^+ and Na^+. After sample injection, the sample splits into the coils C_1, C_2 and C_3. The

Table 1
Actual concentration of Li^+ vs. FIA results for artificial serum

Actual conc. (mmol l^{-1})	FIA conc. (mmol l^{-1})	% Deviation
0.500	0.503	0.60
0.700	0.701	0.14
0.800	0.795	0.63
0.900	0.902	0.22
1.000	1.005	0.50

output reading for Li^+ was taken from the sample portion in C_1. When all the sample in C_1 had passed through, the filter knob was turned from Li^+ to Na^+ within 10 s and the instrument zeroed again to obtain a stable baseline as the carrier stream passed. The sample portion in C_2 reached the detector 5 s later and a reading was taken for Na^+. When the sample in C_2 had passed through, the filter knob was turned from Na^+ to K^+ within 10 s and the instrument zeroed again. The sample portion in C_3 reached the detector 10 s later and a reading was taken for K^+.

The artificial sera [2] containing the different concentrations of Li^+, K^+ and Na^+ were injected, after ten-fold dilution, to determine the ions with the FIA system in order to compare the FIA results with the actual known concentrations in the artificial sera. Percentage deviation and correlation curves [12] were used to compare the two sets of values.

The eight different natural sera were then injected and the ions determined by the simultaneous FIA method.

Table 2
Actual concentration of Na^+ vs. FIA results for artificial serum

Actual conc. (mmol l^{-1})	FIA conc. (mmol l^{-1})	% Deviation
138.0	136	1.1
140.0	141	0.57
142.0	142	0.14
144.0	145	1.0
146.1	146	0.34

Table 3
Actual concentration of K^+ vs. FIA results for artificial serum

Actual conc. (mmol l^{-1})	FIA conc. (mmol l^{-1})	% Deviation
3.000	3.02	0.67
3.500	3.50	0.11
4.000	4.00	0.03
4.500	4.49	0.22
5.113	5.25	2.7

3. Results and discussion

The i.d. of the tubings used was 1.0 mm. Optimised coil lengths were found to be $C_1 = 6.0$ cm, $C_2 = 100$ cm, $C_3 = 210$ cm, and the differences between the times when sample portions reached the detector were C_1 to $C_2 = 15$ s and C_2 to $C_3 = 20$ s. The dispersions in the coils were $D_1 = 3.46$ (limited dispersion), $D_2 = 13.2$ (about medium dispersion) and $D_3 = 25.7$ (large dispersion). After considering the relative sensitivities of the flame photometer for the ions Li^+, Na^+ and K^-, the allocations of the coils to the ions were C_1 for Li^-, C_2 for Na^+ and C_3 for K^+ so as to enhance the sensitivity of the flame photometer for all three ions. The residence times (T) for coils C_1, C_2 and C_3 were $T_{C1} = 8.0$ s, $T_{C2} = 31$ s and $T_{C3} = 100$ s.

For FIA, the optimum sample volume range was 80.0–120 μl whilst the batch method required 9.0×10^3 μl (9.0 cm^3) for three ions. Thus, the FIA sample volume was about 1/110 to 1/75 times smaller than that required for the batch technique. The optimum flow rate obtained and used in the process was 5.0 ml min^{-1}. The FIA sampling rate was 108 samples per hour whilst that of the batch technique was 10.5 samples per hour. Thus, the FIA method was 10.3 times faster than the batch technique. Data obtained for each ion in various standard solutions were quite reproducible and calibration plots were considerably linear, showing that the FIA design was reliable. FIA results compared with actual known concentrations of ions in artificial blood sera are shown in Tables 1–3. The correlation plots of actual concentrations versus FIA concentrations were

Table 4
Batch and FIA results for natural sera

Blood serum	Li^+ conc. (mmol l^{-1})			K^+ conc. (mmol l^{-1})			Na^+ conc (mmol l^{-1})		
	Batch	FIA	% Deviation	Batch	FIA	% Deviation	Batch	FIA	% Deviation
1	0.001	0.0011	10	3.80	4.00	5.3	144	142	0.90
2	0.002	0.002	0.00	3.70	3.40	8.1	135	134	0.96
3	0.001	0.001	0.00	3.75	3.40	9.3	110	107	2.7
4	0.000	0.000	0.00	3.90	3.80	2.6	120	118	2.1
5	0.002	0.002	0.00	3.50	3.00	14.0	130	30	0.08
6	0.002	0.0019	5.0	3.30	3.00	9.1	121	20	0.91
7	0.003	0.0029	3.3	4.80	4.72	8.0	130	134	2.8
8	0.000	0.000	0.00	4.00	4.0	0.00	122	122	0.41

straight lines passing through the origin with slopes of 0.99, 1.40 and 0.98. These results show the reliability and acceptability of the simultaneous FIA design.

The batch and FIA results of eight natural sera and the percentage deviations are shown in Table 4. The Li^+ concentrations for the eight natural sera were obtained after the added lithium was subtracted from the total lithium concentration.

4. Conclusions

FIA results for the artificial blood sera were quite similar to the actual known concentrations of ions. Also, FIA results for the natural blood sera were quite similar to those obtained with the batch technique.

The FIA method was 10 times faster than the batch method and required a sample volume that was 1/110 to 1/75 times smaller that that for the batch technique. Hence the FIA method saved time and sample.

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