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Sequential injection with lab-at-valve (LAV) approach for potentiometric determination of chloride☆

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Abstract

Sequential injection with "Lab-at-Valve (LAV)" approach is demonstrated for potentiometric determination of chloride. The LAV flow-through electrode system consists of two Ag/AgCl electrodes: one as a reference electrode, silver chloride activated surface-silver wire soaked in a constant-concentration chloride ion solution in a small tube covered with a polymer-membrane, another as a working electrode (a similar silver chloride activated surface-silver wire) placed in a flow channel. The electrode system is attached at one port of a 10 port multiposition valve. A modified autoburette was used as a propelling device. Using SI operation via a program written in-house, based on LabVIEW®, a standard/sample is inserted, via the selection valve, in potassium nitrate as an electrolyte and water is used as a carrier. The zones are transported from the holding coil to the flow cell to monitor the difference in potential due to concentration cell behavior. The potential difference is then recorded as a peak. Peak height is proportional to logarithm of chloride concentration. The SI-LAV for chloride determination is very simple, fast, precise, accurate, automatic and economical. Applications to mineral drinking water and surface water have been made. The results agree with those of IC and titrimetric methods.

Keywords: Sequential injection; Lab-at-valve; Potentiometry; Chloride.

1. Introduction

Environmental-friendly analytical procedures are in demand for today's analytical chemistry. Green analytical chemistry concerns the use of non-toxic chemicals, with smaller amounts of reagent and hence less waste generated, and with high throughput analysis with a high degree of automation and portability. To meet these requirements, various approaches based on flow analysis have been developed to miniaturize and automate analytical systems, such as flow injection analysis (FIA) [1–3], multi-syringe FIA [4], sequential injection analysis (SIA) [5,6], SIA with lab-on-valve (LOV) [7] and micro total analysis systems (μTAS) or lab on a chip (LOC) [8].

The μTAS concept initiated by the group of the late Widmer [8] in 1990 has become an active research area today. Although, this approach provides fast analysis using minute amounts of sample and reagents, the production of the chip platform needs advanced, expensive facilities, which are not affordable by most laboratories, and the application of the technique to real samples is still limited.

Ruzicka introduced a SI-LOV concept [9] in 2000, to perform wet chemistry at microlitre levels with a relatively large bore conduits, to avoid surface contamination and clogging. The SI-LOV was designed to integrate sample processing channels with a multipurpose flow cell, and machined to perfectly fit on top of a selection valve by replacing a stator

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plate and connection port of the valve. In this way, various analytical processes, namely sampling, sample pretreatment, reaction and separation, and detection, can be incorporated onto an SIA valve. This approach is more tolerant to dirty real samples than chip based approaches.

A simpler approach, SI with lab-at-valve (LAV) concept, has been proposed [10,11]. This is employed by attaching a device integrating sample processing and detection units on a port of a multiposition selection valve, without taking apart components of a purchased valve. This makes the LAV simpler than the LOV. The LAV unit can be built using an ordinary and less precise machine tool, to have suitable functions for chemistries of interest and with a nut that can plug in a port of the valve in the usual way. Such an integrated LAV device compiling analytical process taking place in it should be compact and economical comparing to a normal SIA system. Various advantages similar to those of the LOV should be gained by using the LAV. In this paper we demonstrate SI-LAV approach for potentiometric determination of chloride with a simple made chloride ion selective electrode (ISE), which has been introduced earlier for use in FI [1–3], but with modification to use a Ag rod instead of tubular Ag to make the electrode more easy to clean and replenish the AgCl film, and to store after use. The proposed potentiometric system is simpler than the previously reported spectrophotometric ones and does not require expensive or toxic reagents, e.g., silver nitrate [5] or mercuric thiocyanate [6,7].

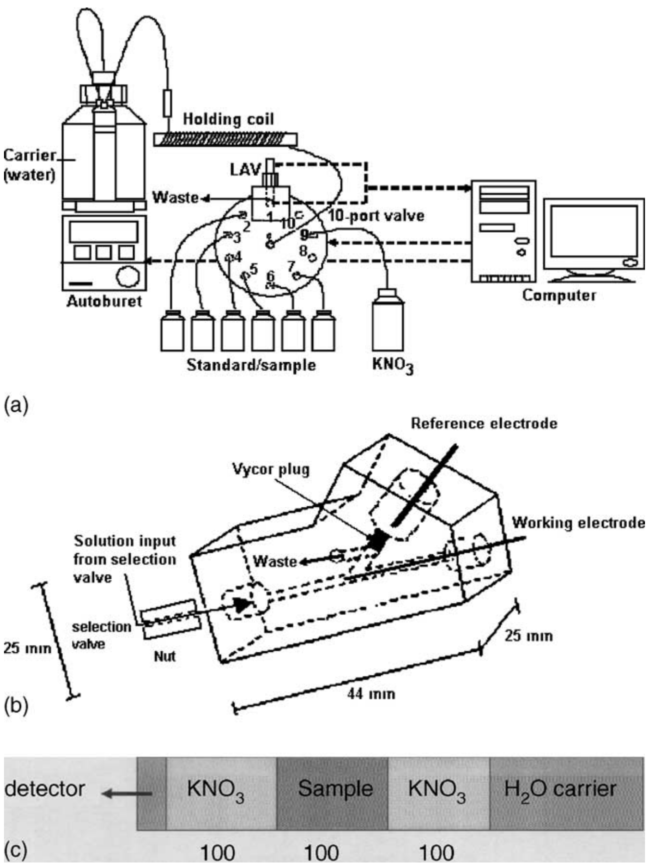

Fig. 1. (a) Schematic diagram of the SI-LAV system; (b) Potentiometric flow cell (LAV unit), the LAV plugged onto a port of the selection valve (45 mm distance from the port to the working electrode, 1.0 mm i.d. channel); and (c) Sequence of solutions aspirated into the system; the values indicating volumes of the solutions (μl).

2. Experimental

2.1. Chemicals

All chemicals used were of analytical reagent grade. Deionized water (obtained by a system of Milli-Q, Millipore, Sweden) was used throughout. A chloride standard stock solution (0.2 M) was prepared by dissolving 5.8440 g of sodium chloride (Merck, Darmstadt, Germany) in water and making upto a volume of 500 ml in a volumetric flask. Working standard solutions of appropriate concentrations were obtained by diluting the stock solution with water. A potassium nitrate stock solution (0.10 M) was prepared by dissolving 5.05 g of potassium nitrate (Merck, Darmstadt, Germany) in 500 ml of water. Working electrolyte solutions of appropriate concentrations were prepared by diluting the stock solution with water. A ferric chloride solution (0.5 M) in 1 M hydrochloric acid was prepared by dissolving 8.11 g of $FeCl_3$ anhydrous (Merck, Darmstadt, Germany) in 100 ml of 1 M HCl.

2.2. Potentiometric flow through cell

A potentiometric flow through cell was designed to be put on a side of a selection valve by plugging into one port of the selection valve (the cell acts as the LAV unit) as shown in Fig. 1(a). The cell was made from a Perspex plastic block (see Fig. 1 (b)) by cutting and drilling to form channels for inserting a Ag/AgCl wire working electrode (WE) and another Ag/AgCl wire reference electrode (RE), and for carrier solution inlet and outlet. The channel for RE was separated from the carrier solution channel by a small VYCOR plug (BAS, Indiana, USA), acting as a salt bridge.

2.3. SI-LAV manifold

The SI-LAV system used is schematically depicted in Fig. 1(a). It consisted of an autoburette (765 Dosimat, Metrohm Ltd., Herisau, Switzerland) equipped with a 10 ml exchange unit for the pumping system, connected to a personal computer via an RS232C interface, a ten-port multiposition valve with a microelectric actuator (C25-3180EMH, VICI, Texas, USA), and a LAV unit with two Ag/AgCl electrodes, which are connected directly or via a potentiometer (744 pH meter, Metrohm Ltd., Herisau, Switzerland) to the input terminals of a data acquisition board (AT-MIO-16X-50 equipped with SCB-68, National Instruments, Texas, USA). The autoburette was connected to the center of the selection valve via a holding coil (Tygon®tubing, 0.8 mm i.d., 4.0 mm o.d., 4.5 m long, Cole-Parmer Instrument Company, Illinois, USA) and the LAV unit was placed at port-1 of the selection valve. Both instrumental control and data acquisition were manipulated via programs written in-house based on LabVIEW®software (Version 6; National Instruments, Texas, USA). This software provided control of the volume to be dispensed or aspirated by the autoburette, flow rate, selection of different valve positions and performance of data acquisition. The SIA-gram data were evaluated for peak height by using Microsoft® Excel 97 software (version 8.0, Microsoft, Arizona, USA).

2.4. *Preparation of a Ag/AgCl electrode*

A silver wire (0.5 mm in diameter) obtained from a local jewelry shop was used to prepare an Ag/AgCl electrode. The wire was polished and cleaned just before immerging it into a solution of 0.5 M ferric chloride in 1 M hydrochloric acid, to form a AgCl film on the electrode. The electrode was then washed with water and used as a working or a reference electrode by assembling each into the flow through cell described above. A VYCOR plug served as a salt bridge for the reference electrode, and the reference electrode was immersed in 1.40 mM KCl/0.01 M KNO_3 solution, unless otherwise stated.

2.5. *Procedure*

The solution aspiration sequence of the SI-LAV system is summarized in Table 1 and Fig. 1(c). First, the carrier (H_2O) was drawn to fill all tubes. Then, a 100 μl portion of potassium nitrate, 100 μl of standard/sample and 100 μl of potassium nitrate solution, respectively, were sequentially aspirated into a holding coil. Finally, the stacked zone was sent to the LAV unit to monitor for potential difference between WE and RE as the zone passed the WE, recording as a SIA-peak. The potential difference is based on a concentration cell, a difference in concentrations of chloride in the WE and RE half-cells. A calibration graph was plotted of the peak height obtained as a function of the logarithm value of concentration of the chloride standard. Chloride concentration in a sample was evaluated from the calibration graph. In spite of the slow operation of the autotitrator, the whole operating cycle took only about 70 s for a sample. Replacing with a more efficient pumping device would result in even a higher sample throughput.

3. Results and discussion

3.1. *SI-LAV components*

The SI-LAV concept was demonstrated for the determination of chloride. A LAV unit, a flow through cell for potentiometric detection with a simple home-made chloride ion selective electrode, could be fabricated small enough to put at one port of the selection valve (see Fig. 1). The upper port position was the most appropriate one to attach the flow cell to the valve because it is easier to remove any air bubble, which may be in the line out of the cell. A polymer VYCOR plug was inserted between the reference electrode and the flow channel in order to prevent leaking of chloride from the reference solution. The LAV is compact in size and has various advantages that are similarly offered by a LOV system [9]. However, the LAV can be assembled without taking apart components of a purchased valve and is easy to build to be suitable for chemistries of interest. Moreover, it can be fabricated with relatively low-cost, less precise machine tools. In this work, an autoburette was employed as an alternative inexpensive solution propelling device in place of a syringe pump. However, a solution volume of less than 100 μl cannot be aspirated due to the default setting of the autotitrator to aspirate at least 100 μl volumes each time. The WE and RE were connected directly to the signal and ground poles, respectively, of an analog input of the interfacing board. Identical signal profiles were obtained by either connecting the electrode directly to the input of the interface card or by inserting a potentiometer between them. This indicates that an impedance of the interfacing board input terminal was high enough to detect the cell potential correctly.

3.2. *Optimization*

Due to limitation of the autoburette used, some parameters were fixed: volume of electrolyte solution and sample, 100 μl each, flow rate for aspiration and dispensation of the solution, 15 ml min^{-1}. The effects of concentration of the electrolyte (KNO_3) solution and sodium chloride in the RE half cell on the slope of the calibration graph for chloride were investigated. It was found that the electrolyte concentration did not significantly affect to the slope, intercept and R^2 of the calibration graph, for the injection of a series of standard solutions as shown in Table 2. However, the 0.01 M KNO_3 was selected to minimize the effect of ionic species due to

Table 1
SI-LAV operating sequence

Step	Operation	SV port[a]	Volume (μl)	Flow rate (ml min^{-1})	Flow direction
1	Aspirate electrolyte solution	9	100	15	To HC
2	Aspirate standard/sample solution	2–7	100	15	To HC
3	Aspirate electrolyte solution	9	100	15	To HC
4	Dispense to LAV unit and record signal	1	2000	15	To LAV

[a] SV = Selection valve.

Table 2
Effect of potassium nitrate concentration

[KNO_3] (M)	Calibration equation (0.60–2.80 mM Cl^-)	R^2
0.005	$y = 0.053x - 0.047$	0.999
0.010	$y = 0.051x - 0.029$	0.999
0.025	$y = 0.049x - 0.038$	0.998
0.050	$y = 0.053x - 0.045$	0.999
0.100	$y = 0.051x - 0.045$	0.999

sample matrices, which may affect the total ionic strength of the solution passing through the WE. For mineral drinking water and surface water samples, this concentration of the electrolyte is sufficient for control of ionic strength of the sample.

Chloride concentration in the reference half-cell did not affect to the slope, intercept and R^2 of the calibration graph (a plot of peak height (V) (y) versus log (mM concentration of chloride standard solution) (x)). Using a reference solution containing 0.01 M KNO_3 with 0.30, 0.80, 1.40 or 2.80 mM potassium chloride, the calibration equations: $y = 0.051x - 0.030$, $R^2 = 0.998$, $y = 0.051x - 0.032$, $R^2 = 0.998$, $y = 0.051x - 0.032$, $R^2 = 0.999$ or $y = 0.051x - 0.030$, $R^2 = 0.998$, respectively were obtained. A 1.40 mM chloride solution with 0.01 M KNO_3 in the RE half cell was selected.

3.3. Analytical characteristics

Three linear calibration graph ranges, 0.10–0.80 mM ($y = 0.059x + 0.120$), $R^2 = 0.998$), 0.80–8.40 mM ($y = 0.056x - 0.105$, $R^2 = 0.998$) and 10–120 mM ($y = 0.060x - 0.128$, $R^2 = 1.000$) were obtained. Each injection consumed 200 μl of 0.01 M KNO_3 and 100 μl of standard/sample, with the whole analysis time of 70 s, which corresponds to sample throughput of about 50 h^{-1}. Relative standard deviations for 11 replicate injections of 10–40 mM chloride standards were in range of 0.7–1.3%. Higher %RSDs may be obtained for solutions containing chloride concentrations out-side of the range.

The stability of the electrode was studied by continuous injection (about 300 injections) of a series of concentrations of chloride standard solutions (0.10–0.80 mM) and some samples, for a period of time about 6 h. The slope of the calibration graphs was quite constant (0.06 ± 0.01), indicating a good stability of the electrode for at least 6 h. Although, the effects of some interferences have not been investigated here, the literature [12–14] indicates that some halides (I^- and Br^-), sulfide, cyanide and some metal ions (Fe^{3+} and Al^{3+}) have some interferences in the analysis by this kind of chloride ion selective electrode. However, these ions are usually present in natural waters at relatively low concentrations compared to chloride and do not significantly interfere, otherwise sample pretreatment is needed [12–14].

Table 3
Chloride contents in mineral drinking water (triplicate determination)

Sample	Chloride concentration (mM)	
	IC [15][a]	SI-LAV[b]
1	0.30	0.37 ± 0.01
2	0.14	0.15 ± 0.01
3	0.65	0.73 ± 0.02
4	0.37	0.35 ± 0.01
5	0.08	<0.10
6	0.06	<0.10
7	0.02	<0.10
8	0.02	<0.10
9	0.17	0.20 ± 0.01
10	2.36	2.26 ± 0.01
11	0.02	<0.10

[a] Analysis by routine laboratory of the Science and Technology Service Center, Faculty of Science, Chiang Mai University.

[b] Using the calibration equation of the range 0.10–0.80 mM Cl^-. The limit of quantitation is 0.10 mM.

Table 4
Chloride contents in surface water samples taken around a pickling industry (triplicate determination)

Sample[a]	Chloride concentration (mM)	
	Titration [16]	SI-LAV[b]
1	3.0 ± 0	2.0 ± 0.3
2	86 ± 1	86 ± 1
3	85 ± 2	86 ± 2
4	86 ± 3	88 ± 1
5	66 ± 0	69 ± 1
6	66 ± 1	68 ± 1
7	71 ± 2	71 ± 2
8	50 ± 1	45 ± 2

[a] Sample 1 = supplied pond water for the factory usage, 2–8 = surface water around the factory.

[b] Using the calibration equations of ranges of 0.80–8.40 and 10–120 mM Cl^-.

3.4. Application to water samples

The developed SI-LAV system was applied for the determination of chloride in different commercially available mineral drinking water samples from a market place in Chiang Mai, and surface water samples collected from around the vicinity of a pickling factory in Hang Dong district of Chiang Mai. Analyses by ion chromatography [15] and Mohr titration [16] were also carried out for comparison. The results (means of triplicate determinations) obtained are summarized in Tables 3 and 4. The results from the pairs of the two methods correlate well with each other, except at low concentrations of chloride. However, the t-test at 95% confidence level indicated that the results obtained from the techniques are not significantly different [17]. The chloride contents in surface water around the pickling factory were found to be significantly higher than the raw water used by the factory, indicating that salt may be introduced to the surface water via discharge water. More close investigation on this will be carried out in our laboratory.

4. Conclusion

A novel SI-LAV concept is demonstrated. Here we describe potentiometric determination of chloride in some water samples. Various advantages of the proposed LAV are similar to those of the LOV, such as economical and integrated instrumentation, small amounts of reagent consumption, rapidity, and automation in analysis. However, the LAV unit can be more easily fabricated with relatively low price materials and available instrument/machine tools, so the LAV could be a cost effective alternative. Other LAV developments such as solvent extraction and bead injection are in progress [18,19].

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