Sequential injection system for simultaneous determination of chloride and iodide by a Gran’s plot method

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Abstract

This paper describes an automated set-up based on the sequential injection analysis (SIA) concept with potentiometric detection for the determination of chloride and iodide at low concentrations. The assessment of both ion concentrations is accomplished by titration with silver ions using the Gran’s plot approach. The proposed procedure enables chloride and iodide to be determined simultaneously in the range 6.0 × 10−6 to 1.0 × 10−4 mol l−1 if a minimum silver concentration in the volumetric solution is chosen (5 × 10−5 mol l−1). Conventional titrations based on the first derivative evaluation of the equivalence points applied to the same solutions fail, especially for chloride determinations. Although, a comparison of results obtained for higher analyte concentrations shows that they have similar accuracy and precision.

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1. Introduction

The field of titration procedures is the oldest yet an accurate tool to perform analyte determinations in samples. However the demands for time saving and scale-down in order to reduce reagent consumption and analysis costs have encouraged the development of different automated titration procedures. In this context, flow-based procedures contributed to fullfil these goals. The titration procedure has been adapted to flow technology since Bladell and Laessig [1–3] proposed a system in which a continuous or variable addition of the analyte to a constant flow of the volumetric solution was monitored by means of a potentiometric sensor until the correct analyte flow rate enabled the stoichiometric ratio. The use of a mixing chamber allowed complete homogenisation between both solutions and a prior calibration procedure was necessary to correct results biased by drifts in the flow conditions.

With the advent of flow injection analysis [4], several tentative procedures were proposed in order to perform titrations under controlled dispersion conditions. In the more common approach, the logarithm dependence of two pseudo end-points found in the front and tail of the gradient created by injection of sample in the flow stream is used to establish a relationship between the time difference between the two events for several calibration solutions and the corresponding concentration. Korn et al. proposed a flow set-up based on a binary sampling concept [5] where the analyte and volumetric solutions were aspirated through the same pumping channel and mixed in a non-segmented stream. The volumetric ratio between the analyte and volumetric solutions necessary to achieve the titration end-point was not dependent on the current hydrodynamic conditions and thus calibration procedures, which are not involved in conventional titrations were also avoided.

In the present work this concept was used in a potentiometric multi-task flow system based on the sequential injection analysis (SIA) concept [6] to provide automated calibration and on-line preparation of testing solutions. Gran’s plots enable linearisation of data obtained in
potentiometric titrations and thus easily and precisely to locate equivalence points of titrations. The theory associated with these plots is straightforward [7]. The response of an ion-selective electrode to a single charged cation, $X$, in solutions free from interferents, may be represented by the Nernst equation:

$$E = E^0 + S \log a_X$$

where $S$ is the slope of the electrode response plot and $a_X$ is the activity of the monitored ion in the sample solution. Rearrangement of this equation gives:

$$\text{antilog} \left( \frac{E}{S} \right) = \text{constant} (a_X)$$

where constant is $\text{antilog}(E_0/S)$. Hence, $\text{antilog}(E/S)$ could be plotted against the volume of the analyte added to give a linear plot with an intercept on the analyte volume axis $a_X = 0$ corresponding to the equivalence point if correction for the volume of analyte added is made. Important advantages of Gran’s plots result from the use of several experimental data obtained farthest from the equivalence point, which are insensitive to interferences that produce a separation between end-point and equivalence point. They also save time in producing reliable results even when performed under flow conditions [8].

Potentiometric determinations of chloride or iodide in flow conditions have previously been described [9–14] but could not discriminate between more than one halogen species. In this work it is proved that if more than one analyte is present in the sample to be titrated and both analytes are present at low concentrations, the Gran’s plots approach could provide good analytical results, even when conventional first derivative titrations fail. However, the analytical ranges of the analytes and the volumetric solution concentrations should be carefully selected.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared with distilled, deionised water (conductivity <0.1 $\mu$S cm$^{-1}$). Analytical grade chemicals were used without further purification. Potassium iodide, sodium chloride, potassium nitrate and silver nitrate (Merck) were used throughout. The iodide stock solution of 0.1 mol l$^{-1}$ was prepared from solid potassium iodide (Merck, ref. 1.09990) by careful dilution with water. The less concentrated solutions ranging from $5.0 \times 10^{-6}$ to $5.0 \times 10^{-3}$ mol l$^{-1}$ were further diluted with 0.1 mol l$^{-1}$ potassium nitrate.

A 0.1 mol l$^{-1}$ silver nitrate stock solution for the potentiometric determination was prepared from Titrisol vials (Merck, ref. 1.09990) by careful dilution with water. The less concentrated solutions ranging from $5.0 \times 10^{-6}$ to $10^{-4}$ mol l$^{-1}$ aluminium nitrate in the sample were obtained by adding the stock solution to the prepared sample solution in order to evaluate and avoid co-precipitation.

To determine chloride and iodide ions with potentiometric detection a carrier solution of 0.1 mol l$^{-1}$ potassium nitrate was used. A concentration of $1.0 \times 10^{-5}$ mol l$^{-1}$ of silver ions was maintained in the carrier solutions throughout calibrations of electrodes in order to minimise the baseline drift. Aluminium nitrate stock solution of $1 \times 10^{-2}$ mol l$^{-1}$ was prepared by weighing the solid aluminium nitrate and dissolving it in water. Concentrations ranging from $5 \times 10^{-5}$ to $10^{-4}$ mol l$^{-1}$ aluminium nitrate in the sample were obtained by diluting the stock solution in the aforementioned manner.

2.2. Electrode preparation

Tubular silver-selective electrodes with a homogeneous crystalline membrane and without internal reference solution were constructed as previously described [15]. The electrode membranes were maintained in contact with $1.0 \times 10^{-3}$ mol l$^{-1}$ silver solution for about 12 h. The electrodes were kept in contact with the same solution after they were polished.

This sensor module was firmly attached to the set-up, inserted into an acrylic rectangular block and screwed on tightly. That allowed the insertion of the electrode into the SIA manifold. The quality of the joint between the flanges which were slotted into it. Hence, the approximately 0.4 mm long sensor surface of the tubular detectors in contact with the solutions had the same diameter as that of the flanges which were slotted into it. The SIA manifold tubes had the same diameter as that of the SIA manifold tubes. From time to time, the membrane of the sensor modules was polished introducing damp cotton and 3 $\mu$m aluminium oxide powder (Buehler, 40-6603-030-016) into the channel. Whenever the detectors were not used for prolonged time periods or showed some loss of their operating characteristics, specially their response rate, they were re-polished and re-conditioned in the aforementioned manner.

2.3. Apparatus

The proposed system used for the simultaneous determination of chloride and iodide by SIA is depicted in Fig. 1. It comprised a Gilson Minipuls 3 peristaltic pump (Villiers-le-Bel, France) as the propulsion device equipped with a PVC pumping tube (i.d. 1.60 mm) of the same brand and a VICI Cheminert C25-3118 E model eight-port selection valve (Valco Instruments, Houston). All tubular flow paths were made of 0.8 mm i.d. PTFE tubing. A holding coil (HC) placed between peristaltic pump (P) and selection
Fig. 1. Schematic view of sequential injection (SIA) set-up developed: P, peristaltic pump; SoV, solenoid valve; HC, holding coil; SeV, selection valve; GE, grounding electrode; IE, indicator electrode; Ref, reference electrode; W, waste.

valve (SeV) was 350 cm long and was coiled over a plastic net. Port 3 of the SeV was connected to a NResearch 161 T031 (Stow) three-way solenoid valve (SoV) by means of a 9 cm long tube.

A potentiometric detection unit was connected to port 8 with a 55 cm long tube. The Ag(I)/Ag_2S tubular electrode with a homogeneous crystalline membrane sensitive to silver ion, constructed according to Ferreira et al. [10], was used as the potentiometric detector with a AgCl/Ag double-junction reference electrode from Russell, model 90-0029, containing 10% potassium nitrate solution in the outer compartment.

Potentiometric measurements were made with a Crison Model 2002 digital voltmeter (±0.1 mV sensitivity) and titration curves recorded with a Kipp and Zonen model BD 111 chart recorder. The other inlets of SeV and SoV_2 were fitted with 18 cm long PTFE tubing. SoV_1 was positioned between the peristaltic pump and the HC in order to minimise the inertial effect of the fluids and to discard pulses which affected the reproducibility of the volumes aspirated into the system. This valve enabled the flow of the fluids inside the HC to be synchronised with the peristaltic pump movement [16].

Several laboratory-made devices, namely joints, the support of the reference electrode and the earth connection contact (ground electrode) as well as the support of the silver-selective tubular electrode (construction described elsewhere [17,18]) were also used. The rotation speed of the peristaltic pump, the rotor position for the SeV and SoV_2 were controlled through a PCL-711 Advantech interface card and laboratory-made software was developed in Quick Basic 4.5 language.

An automated system for conventional potentiometric titration comprised a Crison 2031 burette and Crison 2002 pH-meter, both computer controlled. An AgCl/Ag double-junction reference electrode from Russell, model 90-0029, containing 10% potassium nitrate solution in the outer compartment was used as a reference electrode and a silver-sensitive electrode of conventional shape [15] was applied as an indicator electrode.

### Procedures

Initially, the holding coil and transmission line between SeV and the detection system were filled with the carrier solution, selecting port 8 of SeV and positioning the peristaltic pump in the propulsion mode. This configuration was kept until a stable detector signal was achieved. Afterwards, the flow direction was reversed and port 4 of SeV was selected in order to fill the respective access channel with the externally prepared calibration solution. Selection of SeV port 3 and activation of SoV_2 enabled filling of the inlet channel with silver nitrate in order to titrate and to estimate the electrode slope.

When port 3 was selected and SoV_2 was inactive, the channel of the passive port was filled either with the sample solution to enable the potentiometric titration, or with the carrier solution to promote the calibration of the potentiometric detection unit. After the solutions reached the HC, they were discharged to waste by selecting SeV port 5 and driving the pump in the forward mode.

The analytical cycle established for the potentiometric determination of chloride and iodide comprised five steps (Table 1). By sequential performance of the first two steps four times, the calibration of the electrode becomes possible in order to determine its response slope. In each of these cycles, 928 μL of externally prepared solutions containing 1.0 × 10^{-5}, 5.0 × 10^{-4}, 1.0 × 10^{-3} or 5.0 × 10^{-3} mol L^{-1} of silver nitrate were aspirated inside the system by means of port 4 of the SeV. Afterwards these plugs were sent to the detection system with a flow rate of 2.6 ml min^{-1} selecting port 8 of SeV and using the peristaltic pump in the forward pumping mode. The titration cycle was performed by

<table>
<thead>
<tr>
<th>Step</th>
<th>Task</th>
<th>SeV state</th>
<th>Volume (μL)</th>
<th>Flow rate (ml min^{-1})</th>
<th>Time (s)</th>
<th>Flow direction (FR)^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sampling</td>
<td>4</td>
<td>-</td>
<td>927</td>
<td>2.78</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>Detection</td>
<td>8</td>
<td>-</td>
<td>6068</td>
<td>2.60</td>
<td>140</td>
</tr>
<tr>
<td>3</td>
<td>Sampling</td>
<td>3</td>
<td>On/off (5–75%)</td>
<td>927</td>
<td>2.78</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>Detection</td>
<td>8</td>
<td>-</td>
<td>6068</td>
<td>2.60</td>
<td>140</td>
</tr>
<tr>
<td>5</td>
<td>HC cleaning</td>
<td>5</td>
<td>-</td>
<td>607</td>
<td>2.60</td>
<td>14</td>
</tr>
</tbody>
</table>

^a Forward (F), reverse (R).
selecting port 3 and filling SoV active port channel with the volumetric solution and subsequently sending it to waste.

Volumetric solution aliquots intercalated with sample aliquots were inserted into the HC by means of on/off cycles of SoV2 when a set of electric pulses was sent to SoV. To accomplish this, small aliquots of the volumetric solution (silver nitrate) were aspirated to the HC by actuating SoV2 (SoV2 on) and intercalated with aliquots of the sample solution (SoV2 off). The mutual dispersion between the aliquots of both solutions throughout aspiration to the HC and sending of both zones to the detector enabled the titration to be carried out. To accomplish the titration procedure, the time interval to switch SoV2 on was set to 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70 and 75% of each SoV2 on/off cycle period (t1).

Before sample injection, calibration with standard solutions of different silver concentrations was carried out. For very low concentration of volumetric solution and sample, it was necessary to determine the slope of the electrode response under the same conditions as those used during the titration program (Table 1, steps 3, 4 and 5), with volumetric solution at the active port of SoV2 and carrier at the passive port of SoV2.

Some preliminary experiments were performed to establish the flow injection parameters to evaluate the tubular electrode characteristics. Determinations of chloride and iodide were also carried out by conventional potentiometric titration using conventional silver-selective electrode as indicator and silver nitrate as volumetric solution. This determination was performed with an automated batch titrator. The equivalence point was determined using the first derivative of the titration curves. The potentiometric titration was performed with variable volume additions of volumetric solution ranging from 0.001 to 2.0 ml, using concentrations of volumetric solution varying from 5.0 × 10^{-5} to 10^{-3} mol L^{-1}. The initial addition of volumetric solution was set to 0.005 ml. Volumes of analytic solutions were selected between 5.0 and 15.0 ml. The time period of constant potential before the next addition was set at 5 s.

3. Results and discussion

3.1. Set-up optimisation

The described SIA set-up was optimised, assessing the influence of the hydrodynamic and chemical parameters on the peak height, reproducibility and accuracy of the results. After initial trials for selection of approximate values for each parameter, optimisation of various experimental conditions of the flow system, such as injection volumes, flow rate, sampling rate and switching time of SoV2, were investigated and established using an univariate search approach.

This study was initially started with 5 × 10^{-2} mol L^{-1} solution of silver ions. Then the flow rate was assessed in the interval 2.6–5.9 ml min^{-1} and it was found that higher sensitivity was obtained with lower flow rates, although the sampling rate suffered from a great decrease. A flow rate of 2.6 ml min^{-1} was selected for the measurement step, under which conditions maximal response was attained. Thereafter, several experiments were performed with aspiration flow rates of 1.46, 1.84, 2.03, 2.41, 2.6, 2.78 or 2.97 ml min^{-1} and SoV2 cycle periods (t1) of 2.0, 3.0 or 4.0 s. Finally t1 was fixed at 4.0 s and the aspiration flow rate was maintained at 2.78 ml min^{-1}.

Having optimised the flow and sampling rate, the effect of injection volume was determined. The effect of sample volume was investigated setting different sampling times and loading an aliquot of an externally prepared silver standard solution of 5 × 10^{-1} mol L^{-1} into the HC (Table 1, step 1) and directing it towards the detector (Table 1, step 2). These two steps were repeated but with larger sampling intervals (9–50 s) with various increments (7 and 10 s, respectively).

By increasing the injection volume up to 927 µl (corresponding to sampling time of 20 s) the analytical signal of silver ions increased. The sampling time was set to 20 s, allowing the resulting signal to correspond to about 95% of steady-state. Using a larger volume (longer sampling time) would produce an undesirable increase in time to return the measured signal to the baseline and only a slight increase in the signal. Smaller volumes produced less reproducible signals.

Experiments to check the overall behaviour involved running a set of externally prepared silver calibration solutions and setting the sampling time interval at 20 s, the flow rate at 2.6 ml min^{-1}, the sampling rate at 2.78 ml min^{-1} and the time of the switching period t1 at 4.0 s. Once the optimal conditions were established, a calibration graph for solutions ranging between 2.5 × 10^{-6} and 0.1 mol L^{-1} was processed to evaluate the linear and non-linear response zones. The calibration graph for the silver-selective tubular electrode was linear between 1.5 × 10^{-5} and 0.1 mol L^{-1} Ag(I) in the injected solution.

3.2. Implementation of the simultaneous titration procedure

Both chloride and iodide ions promote the quantitative reaction with Ag(I) ion, resulting in the formation of a precipitate under stoichiometric conditions. Since the solubility products (Ksp) of the resulting precipitates are quite different, 5.0 × 10^{-10} mol² L^{-2} for AgCl and 2.0 × 10^{-16} mol² L^{-2} for AgI in 0.1 mol L^{-1} ionic strength adjusted media, it should be possible to have two well-defined equivalence points in the titration curves using either conventional batch equipment or the developed set-up (Fig. 2). This aspect enables the sequential determination of chloride and iodide by potentiometry using a crystalline membrane Ag(I)/Ag₂S electrode.

To evaluate the minimum concentration of chloride and iodide that could be determined (taking into account the lower limit of linear response of the electrode) both the first
analyte titrant sample SIA system conventional procedure

results obtained (mol l\(^{-1}\)) by the proposed procedure using the Gran's plot method and by the conventional first derivative method after titration of prepared sample solutions

Table 2 shows the analytical ranges in which both ions could be determined for different concentrations of the volumetric solution. Lower limits correspond to the lowest concentration of analyte solution that are needed to obtain an equivalence point using the proposed procedure. Higher

table was changed to the sequence of ports 3 and 8; this would be repeated twice automatically (Table 1, steps 3, 4 and 5).

to accomplish a halide titration the concentration of silver ions in solution before the equivalence point could be determined considering both the concentration of the anion and the solubility product of the precipitate ([Ag\(^+\)] = \(K_{sp}/(\left[\text{I}^{-}\right] \times \left[\text{Ag}_{\text{ads}}\right])\)). Concentrations are considered instead of activities once the ionic strength is constant. For iodide and chloride it will correspond to concentrations of free silver below the lower limit of linear response. After the equivalence point and using the equation [Ag\(^+\)] = [Ag\(_{\text{ads}}\)] it is possible to calculate the concentration of unbound silver, which determines the analytical signal.

Table 2 shows the analytical ranges in which both ions could be determined for different concentrations of the volumetric solution. Lower limits correspond to the lowest concentration of analyte solution that are needed to obtain an equivalence point using the proposed procedure. Higher
limits were based on the assumption that a minimum of four experimental results after the equivalence point are necessary to estimate them. The accuracy and precision achieved in the titration of different solutions of iodide and chloride is evidenced in Table 3. As can be seen, the increase in volumetric solution (titrant) concentration corresponds to an increase in accuracy of the achieved results together with the increased number of experimental points which define a linear Gran’s plot (Fig. 3).

For the same conditions, conventional titrations provided inaccurate results for iodide determinations because the effect of the curvilinear region of electrode response damps the potential shift of the titration curve. In a chloride titration, this effect is more pronounced due to the greater solubility of the produced silver chloride. For this reason it is impossible to get accurate results.

In the case of the simultaneous titration, an additional difficulty arises since the excess of silver ions after the first equivalence point should be equal to or smaller than the value determined by the chloride precipitation equilibrium in order to provide unbiased results. As can be seen in Table 3 this condition is achieved when the concentrations of both ions are low and do not differ from each other more than one decade.

Several experiments were performed with aluminium nitrate in the sample solutions in the range of $5 \times 10^{-6}$ to $10^{-4}$ mol l$^{-1}$ in order to evaluate its influence on co-precipitation. It was found that for low concentrations of iodide and chloride ($10^{-6}$ to $10^{-5}$ mol l$^{-1}$) its influence on the quality of the results was not significant.

4. Conclusions

The proposed SIA procedure enables low concentrations of chloride or iodide in pure solutions was inaccurate or impossible using the conventional batch titration.

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