

Pulse Amperometric Detection of Salt Concentrations by Flow Injection Analysis Using Ionodes

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A sensitive novel approach of using an amperometric ion detector for the flow injection analysis of salts has been developed. The detection methodology is based on measuring the current associated with the transfer of ions across polarized microinterfaces between the aqueous sample solution and a 2-nitrophenyloctyl ether–poly(vinyl chloride) gel phase, referred to as *ionodes*. Different sodium salts of fluoride, chloride, bromide, nitrate, and sulfate were investigated. It was found that by employing an amperometric pulse detection mode and pure water as eluent, the detection limit of the ionode detector could be lowered to ppt level of salt concentrations under flowing conditions.

Extensive studies employing the interface between two immiscible electrolyte solutions (ITIES) as ion-sensitive detectors have been undertaken in the last past two decades.^{1–8} The most common method to use the ITIES as an amperometric sensor for the detection of nonredox ionic species is performed by measuring the current associated with ion transfer reactions across a polarized liquid–liquid interface. To transform the ITIES to a more convenient detector assembly, much of the recent work has been dedicated to gelify either the aqueous or the organic phase.^{1,4} There have been promising results proving that this type of gel–liquid interface combined with an amperometric methodology referred to as amperometric ion-selective electrode (ISE) can be a powerful transducer for analytical applications. Other approaches using liquid–liquid interfaces supported on hydrophilic and hydrophobic membranes^{9–12} have also been investigated.

Investigations into the use of ITIES as anion sensors in a flow cell have been made by several authors.^{12–14} Results have shown that amperometric ISE can be used as an effective detector for hydrophilic anions such as nitrate, bromide, iodide, thiocyanate, and perchlorate. The transfer reactions for the detection of anions from the water to the organic phase appear at the end of the potential window on the negative side (water vs oil) due to their relatively high Gibbs energies of transfer from water to the organic phase. Some reports have highlighted the direct transfer of anions (e.g., chloride) across the ITIES when a low concentration of supporting electrolytes is used.^{15,16} A possible method to shift the Gibbs transfer energy would be to incorporate ionophores into the organic gel phase. Although there has been some progress showing the specific complexation of anions by selective ionophores, sensitive detection of these anions is still hampered by the relatively low complexation ability of these new compounds when compared to ionophores for cations.^{17–19}

In previous studies,^{20–22} we have demonstrated a reproducible fabrication methodology of liquid–gel microinterfaces, referred to as *ionodes*, and shown promising results of using these interfaces as sensitive as well as selective amperometric sensors with the methodology based on ion-transfer reactions. This detector was also successfully employed in cation-exchange chromatography.²¹

We shall highlight here a new approach employing variable pulse potential modes and pure water as an eluent that results in

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Table 1^a

	salt				
	NaNO ₃	Na ₂ SO ₄	NaCl	NaBr	NaF
(a) slope ($R = E/I$)/ Ω	24.9×10^7	18.2×10^7	11.8×10^7	9.4×10^7	5.7×10^7
(b) resistivity ($1/\sigma$)/cm $\cdot\Omega$	7.1×10^3	5.0×10^3	4.5×10^3	8.3×10^3	4.0×10^3
(c) molar conductivity (Λ_m)/cm ² $\cdot\Omega^{-1}\cdot\text{mol}^{-1}$	121.6	260.2	126.5	128.0	105.5
(d) sensitivity using constant-potential amperometry/ $\mu\text{A}\cdot\text{V}^{-1}\cdot\text{cm}^3\cdot\text{mol}^{-1}$	-0.32	-0.80	-0.52	-1.18	-0.79
(e) $\Delta G_x^{0\text{w-o}}$ /kJ $\cdot\text{mol}^{-1}$	21.8 ²⁴	—	43.1 ²⁴	33.8 ²⁴	57.7* ²⁵
(f) sensitivity using dual-pulse mode/nA $\cdot\mu\text{M}^{-1}$	-0.66	-0.76	-0.43	-0.77	-0.52

^a Key to first column: (a) Slopes representing the resistances obtained from the plots shown in Figure 2 for the various salt samples and (b) the resistivity ($\rho = 1/\sigma$) calculated using the molar conductivity of each salt given in (c). (d) The dependence of the ionode sensitivity on the constant applied potential for the flow injection analysis of 1 ppm concentration of each salt sample. The sensitivity of the detector was normalized as a function of each salt sample concentration. The constant applied potential varied from 1 to -2 V. (e) Standard Gibbs energies of transfer of anions across the interface between water and NPOE taken from the literature,²⁴ except the value denoted by *, which was obtained at the water-1,2-DCE interface.²⁵ (f) The dependence of the ionode sensitivity for the flow injection analysis of each salt sample using dual-pulse mode. The aqueous eluent was water. The concentration varied from 60 nM to 125 μM . Injection volume was 60 μL . Flow rate was 0.6 mL $\cdot\text{min}^{-1}$. Final pulse potential varied from 1 to -1 V.

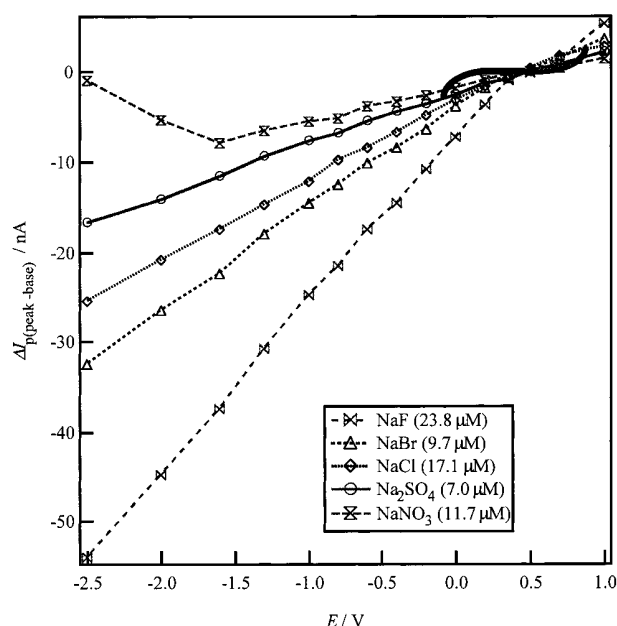


Figure 2. Current responses as a function of the constant applied potential obtained for several salt transfer reactions at the water-PVC-NPOE gel membrane using cell 1. Different sodium salts of fluoride, chloride, bromide, nitrate, and sulfate were used. Each salt concentration, 1 ppm. The aqueous eluent was water. Flow rate was 0.6 mL $\cdot\text{min}^{-1}$. Injection volume was 60 μL . The thick line represents a schematic potential window for cell 1.

As a result of this and the fact that the organic cation concentration is maintained at a fixed value throughout the whole experiment by transfer from the aqueous gel reservoir, the contribution of the cation to the negative detection current is assumed to remain small and constant. Therefore, changes in the measured peak current are mainly due to variations in the sample anion concentration and the applied potential. The linear relationship between the measured current and the applied potential is a direct consequence of the IR contribution. This is also supported by the linear relationship between the resistance (slope (E/I) from Figure 2) and the resistivity of the salt samples given in Table 1a and b, respectively, the only exception being NaBr. Indeed, the ionode detector showed a higher sensitivity toward NaBr salt compared

to the other salts studied at a constant potential (see Table 1d). This particularity is not related directly to the Gibbs energy of transfer, the values of which are given in Table 1e.^{24,25} A possible explanation may be with the solubility or the association constant of TBABr in NPOE which may be different than those of the other salts.

Above an applied potential of 0.2 V, the positive current response corresponding to the transfer of the counterion (e.g., sodium), present in the sample solution, is observed. It was also found that the increase in the positive peak current as a function of the applied potential is less significant than the changes in the negative peak current. Of course, constant-potential amperometry is not an efficient way to operate an ionode and the data of Figure 2 are used thereafter to develop pulse amperometric methods.

Pulse Amperometry. To achieve a better sensitivity of the ionodes and to reduce the effect of a permanent polarization of the interface, a pulse amperometric technique was used. The most used technique for detection in a flow system is pulse amperometry, particularly the differential pulse mode represented in Figure 3a.^{21,26,27} To remove the effect of the baseline current and to reduce the capacitive current effect ($I_{\text{diff}} = I_{\text{pulse}(E_f)} - I_{\text{base}(E_i)}$) a differential mode of this pulse technique is favored. For the optimization of the experimental conditions for the flow analysis of the anions in this work, the effect of the negative pulse potential (see also Figure 3a) on the sensitivity of the ionode detector was studied.

Figure 4 shows the multiple current responses to a flow injection analysis of various concentrations of sodium bromide detected at various negative pulse potentials. The applied pulse potentials were stepped from a base potential of 0.3 V (E_i), where no ion transfer took place, to negative final potentials (E_f) of -0.3, -0.4, -0.5, -0.6, or -1 V, where the transfer of anions mostly occurred (the potential program is given in Figure 4 as an inset). The pulse period was 150 ms, and the current was recorded at the end of the pulse (E_f) (50 ms) and at the end of the base at 0.3

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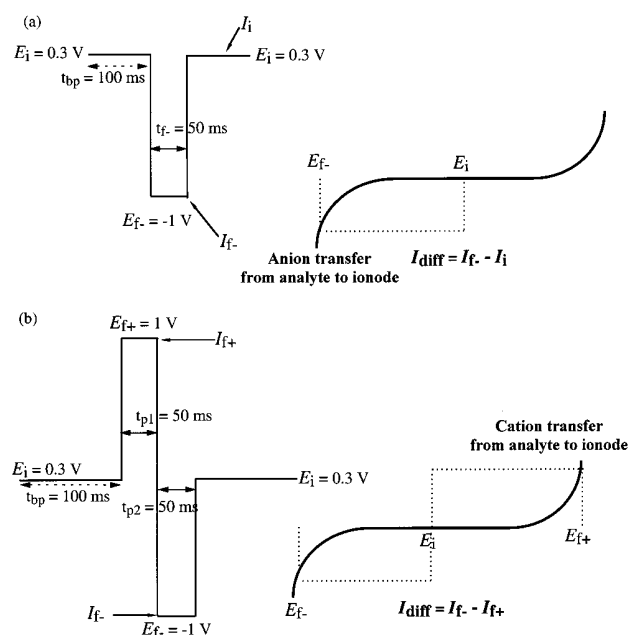


Figure 3. Schematic diagram showing (a) a typical differential pulse amperometry and (b) the dual-pulse amperometry developed in the present work.

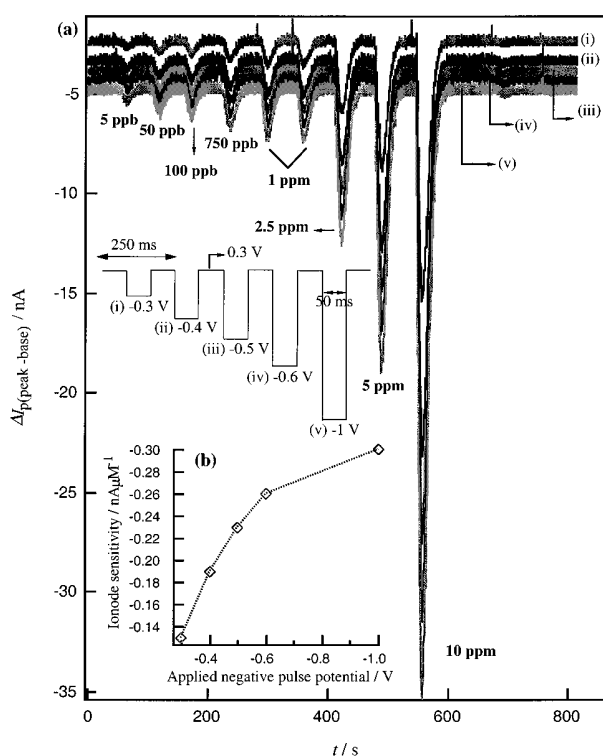


Figure 4. (a) Multiple pulse amperograms obtained for the detection of sodium bromide studied using the PVC–NPOE gel membrane in the absence of the column separation at the various final negative pulse potentials from -0.3 to -1 V . (b) Dependence of the ionode sensitivity on the final negative pulse potential for the flow injection analysis of sodium bromide salt sample. Flow rate was $0.6\text{ mL}\cdot\text{min}^{-1}$. Injection volume was $60\text{ }\mu\text{L}$. The aqueous eluent was water.

V (100 ms). It can be seen that the more negative the pulse potential, the higher the membrane sensitivity toward bromide ions.

The dependence of the ionode sensitivity on the applied final pulse potential is also presented in Figure 4b, showing a nonlinear behavior as compared to Figure 2. For the flow injection analysis of the other salts, a very similar behavior was observed. The concentration dependence of the pulse amperometric response is also not linear and follows that of the constant potential amperometry.

Dual-Pulse Amperometry. In this work, another detection approach, referred to as dual-pulse amperometry, was employed in order to enhance the signal-to-noise ratio. In principle, instead of sampling the current only at the negative limit of the potential window (where the anion transfer is expected to occur), a dual-wave strategy was adopted (where the current was measured consecutively at both the positive and negative limits (see Figure 3b). The difference between the positive and negative currents was measured. Between these dual pulses, the system was rested at a potential (E_i) where no ion transfer took place.

On the basis of the results shown in Figure 4, the potentials of $E_{f-} = -1\text{ V}$ and $E_{f+} = 1\text{ V}$ were chosen as the pulse potentials for the dual-pulse mode analysis. The initial potential was set at 0.3 V where the measured current was almost zero. Parts a and b of Figure 5 show the two components of the measured current (I_{f+} and I_{f-}) at various concentrations of NaBr salt sample solution. It can be seen that there is an increase in the peak current with the concentration of the salt solution injected in the flow system. The increase in the current can be observed both for the positive pulse (E_{f+} and I_{f+}) and for the negative pulse (E_{f-} and I_{f-}) corresponding to the cation and anion transfer, respectively.

From the analysis of the Figure 5, it can also be observed that the negative peak current is higher than the positive peak current, which is in good agreement with the result obtained in Figure 2. No further enhancement of the positive current was achieved by pulsing toward more positive potentials.¹⁶ Consequently, the combination of both waves will take into account both the anion and cation concentrations, resulting in a further improvement of the sensitivity of the detection method. Similar to the case of using the conductivity detector, the dual-pulse strategy employed with the ionodes for the detection of salts can use the total amount of current passed for both cations and anions to enrich the measured signal.

Figure 6a shows an example of a dual-pulse amperogram obtained using the ionode for the flow injection analysis of sodium bromide salt (double injection for various concentrations of the sample) employing a dual-pulse mode with $E_i = 0.3\text{ V}$ and final pulse potentials of $E_{f+} = 1\text{ V}$ and $E_{f-} = -1\text{ V}$. It can be seen that a reproducible and an enhanced sensitive detection for NaBr has been successfully achieved with the relative standard deviation of 0.08.

Figure 6b shows a plot of the ratio of the measured currents as a function of salt sample concentrations. From these results, two aspects can be noticed: (i) There is a considerable improvement of the total peak current ($\sim 160\%$), and (ii) there is no concentration range effect on the linearity of the detection signal when the dual-pulse mode is employed. This contrasts to the other two modes, namely, constant-potential and single-pulse amperometry.

The detection limit (signal-to-noise ratio of 3:1) of the ionode detector measured for the salts studied was found to be $\sim 1\text{ ppt}$.

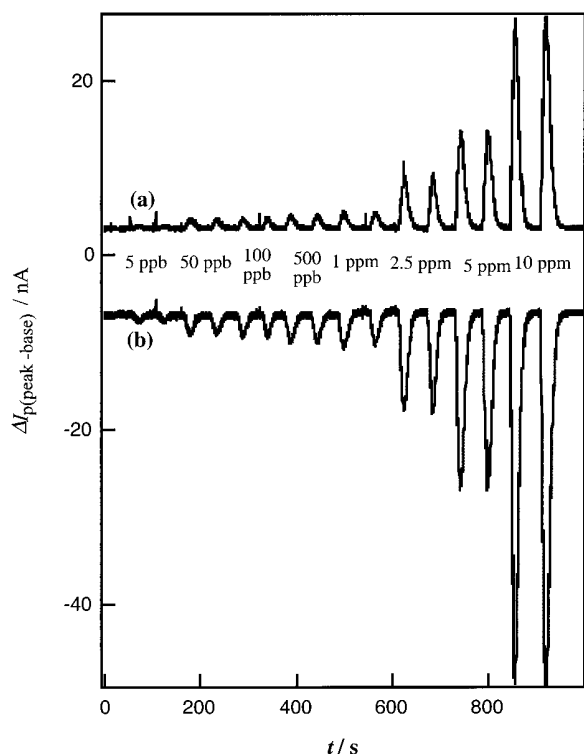


Figure 5. Pulse amperograms obtained for the flow injection analysis of sodium bromide studied using the ionodes at the various concentrations. (a) A pulse amperogram obtained using the initial pulse potential of 0.3 V and the final potential of 1 V. (b) A pulse amperogram recorded using the initial pulse potential of 0.3 V and the final potential of -1 V. The aqueous eluent was water. Flow rate was 0.6 mL·min⁻¹. Injection volume was 60 μL.

Comparing this to results obtained using an eluent consisting of phthalic acid and the pulse mode shown in Figure 3a, the sensitivity of the detector for the flow injection analysis of the different salt samples, using the dual-pulse mode, was enhanced by ~2 orders of magnitude. All the detector responses of the flow injection analysis (mean values of three injections) of various salt samples obtained using the dual-pulse mode shown in Figure 3b are also summarized in Table 1f. It is also worth noting that the durability of one ionode detector was found to be ~100 continuous injections with the standard deviation of 5% and can be used more than a week.

CONCLUSIONS

The experimental results show that the ionodes can be employed as a sensitive detector for the flow injection analysis of single salts. The sensitivity of the ionode detector can be significantly increased by the choice of pulse potentials. By using pure water as an eluent, the detection limit can be decreased to a 1 ppt level concentration of those salts studied. Furthermore,

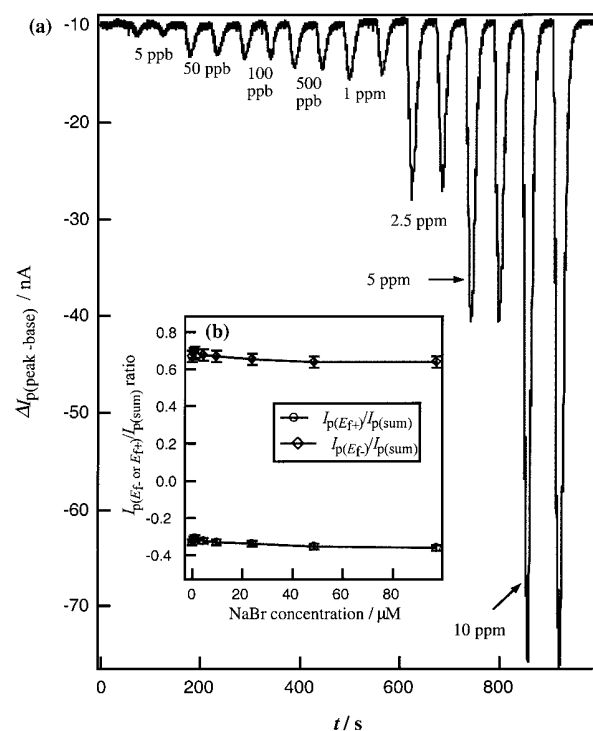


Figure 6. (a) Pulse amperogram achieved using the dual-pulse detection mode for the flow analysis of sodium bromide at the various concentrations. The initial pulse potential (E_i) was 0.3 V and the two final pulse potentials were 1 and -1 V. The aqueous eluent was water. Injection volume was 60 μL. Flow rate was 0.6 mL·min⁻¹. (b) Peak current ratio obtained at between the initial pulse potential of 0.3 V and the final potentials of 1 or -1 V as a function of NaBr concentrations. The data were taken from (a) and Figure 5.

this method does not require any pretreatment of the sample solution such as dilution in the eluent as classically done in ion chromatography with conductometric detection. The methodology presented here provides an alternative to conductometry as a detection method for ion chromatography when a suppressor system is used.

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