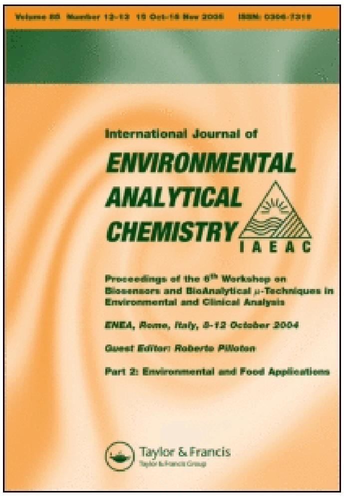

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Josef Lechner[a]; Ivan Sekerka[a]
[a] Canada Centre for Inland Waters, Water Quality Branch, Ontario, Canada

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Automation of Direct Potentiometry†

IVAN SEKERKA and JOSEF LECHNER

Canada Centre for Inland Waters, Water Quality Branch,
Burlington, Ontario, Canada

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A simple, versatile, automated direct potentiometry is described. It offers a wide range of possible applications for all types of ion-selective electrodes, including the glass electrode. The apparatus consists of two Fisher turntable sample changers connected to an Orion automatic switch, Orion pH/mV meter, and Orion printer system via a control module. The optimum sampling rate is 20 samples per hour F^- and NH^+ in water samples were determined by using commercially available ion-selective electrodes.

INTRODUCTION

The idea for automation of direct potentiometric measurements is perhaps as old as the ion-selective electrodes themselves, but it was not until 1969 that Oliver *et al.*[1] introduced a semi-automatic direct potentiometric flow-through system for fluoride analysis in vegetation and gases. Ruzicka and Tjell[2] automated a direct potentiometric flow-through system for calcium; Buck and Reusmann[3] and Svoboda and Ixfeld,[4] produced semi-automated flow-through systems for fluoride analysis in plant and air samples.

However, all of the mentioned methods are basically flow-through systems which possess certain disadvantages in respect to the characteristics of ion-selective electrodes. According to Orion Research Inc.,[5] problems are caused in these systems by the time response of the electrode to step-changes in the concentration of the ion being used.

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The electrode-time response is a function of the magnitude and direction of the concentration change, temperature, and the presence of other ions. As a rule of thumb, the electrode response decreases with lower concentration. It decreases when going from concentrated to dilute solutions and increases when going from dilute to concentrated solutions. The true response at low concentrations, such as those encountered in the field of water analysis, may reach a value of several minutes.

The error created by the electrode-time response can be expressed as the amount, in millivolts, by which a reading at the time of measurement is in error from the steady state reading. The parameters which should be kept constant during measurements involving ion-selective electrodes are: stirring, temperature, and ionic strength of the solution.

To overcome the time response factor the reading of the measurement was delayed after sample-to-sensor contact. The most practical route to achieve this was by automated electrode sample immersion coupled with delayed reading of the potential. To create such a system, Fisher's "Titralyzer" Electrode Elevator Turntable and Orion's "Ion Analyzer" were modified and operated with a programmed control module of our own design.

In general terms, automation of direct potentiometry is an improvement over manual and flow-through systems. Step-by-step actions never vary, assuring equal conditions from the first to the last sample. Automation using this method retains the simplicity inherent in manual direct potentiometry.[6,7] There are no problems with clean-up procedures of the apparatus. The preparation of the apparatus for the measurement of different ions requires only simple manipulation which can be accomplished in a short time. The kinetic parameters of continuous-flow analysis discussed in detail by Thiers *et al.*,[8] except for the time response of ion-selective electrodes, do not apply to automated direct potentiometry.

The operation of the apparatus was verified by the determination of fluoride and ammonia in water samples, using commercially available ion-selective electrodes.

EXPERIMENTAL

Reagents

All chemicals were of reagent grade. Double-distilled water was used for all solutions.

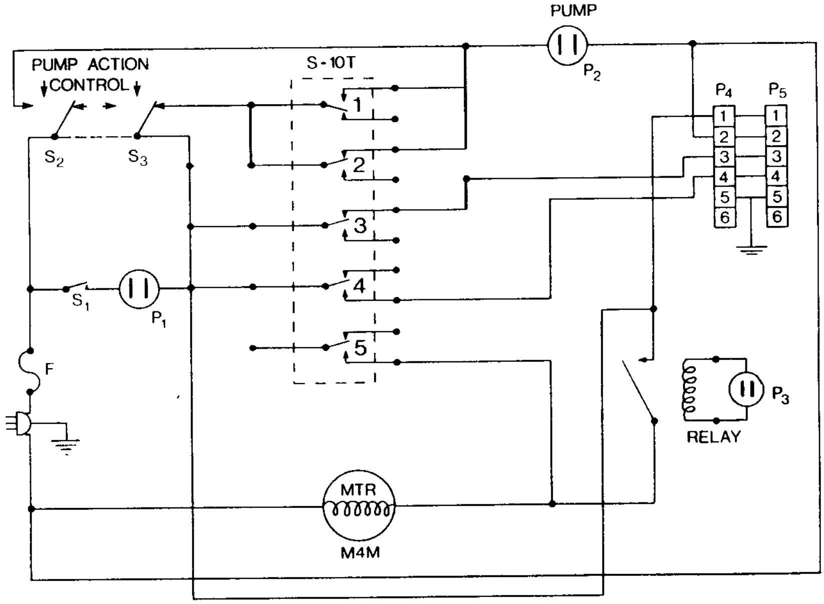
Apparatus

The Orion fluoride electrode Model 94–09 and the Orion combination ammonia electrode Model 95–10 were used in this study. They were prepared according to the manufacturer's directions. All data herein reported were obtained with Orion-801 digital pH/mV meter, Orion-751 digital printer and Orion-855 six-channel automatic switch. The last-mentioned instrument received a minor modification through the installation of two binding posts on the rear panel, which were internally connected to the green, illuminating pushbutton switch power supply near the front panel of channel 5 to provide 24 V DC for triggering the control module at the start of each cycle. The Fisher-9-319-50 electrode-elevator assembly unit was modified by installing a toggle switch ("override") across the upper lever switch. The main power line was then fed through the upper lever switch before applying it to the control module. In this way, all power is cut off as soon as the wedge-shaped steel plate triggers the upper lever switch, provided "override" is in the "off" position. This modification is necessary only for one turntable-assembly unit, if more than one are used in the set up. The incorporation of a Hewlett Packard 7004B recorder with chart advance made it possible to record results directly in ion activity by using semi-logarithmic graph paper with the logarithmic scale on the vertical axis. Direct recording in mg/l was achieved after two-point calibration, eliminating the necessity for calibration curves, and, consequently, the conversion of millivolts to concentration units.

Samples of 50 ml each, in 100-ml Berzelius beakers, were placed into the Fisher turntables Model 9–319–12 which accept 16 samples each. A "Desaga" peristaltic multi-channel pump (Brinkman Instruments) provided the automatic additions of the ionic-strength adjustor. The control module was designed in our laboratory. Its main component is a programmed Mallory Industrial Sequence Timer.[9,10] The electrical diagram is given in Figure 1. All tests were conducted at constant sample and room temperature.

Principle of operation

The apparatus was assembled according to Figure 2. The Orion-855 switch activates the control module, which in turn controls all functions of the turntable assembly and pump. As many as six turntables can be operated simultaneously through the Orion-855 switch and the control module. A circular, water-absorbing paper, fitted between the round-top metal plate and the wedge-shaped metal plate absorbs carry-over liquid drops remaining on the electrodes between sample changes. The elevator, on activation by the control module, lowers the assembly of the electrodes, stirrer and delivery tip into the beakers. On their way down they penetrate the absorbing paper before entering the sample. The delivery tip, through the action of the pump, adds a selected amount of ionic-strength adjustor to the sample. The time-delayed measurement is now in progress.



S_1	*Main switch*	P_2	*To pump*
S_2 S_3	*Pump action control switch*	P_3	*To model 855*
S10T	*Mallory sequence timer*	P_4 P_5	*To turntable*
P_1	*To "Upper Lever Switch"*	M4M	*Motor for sequence timer*

FIGURE 1 Control module for two turntables.

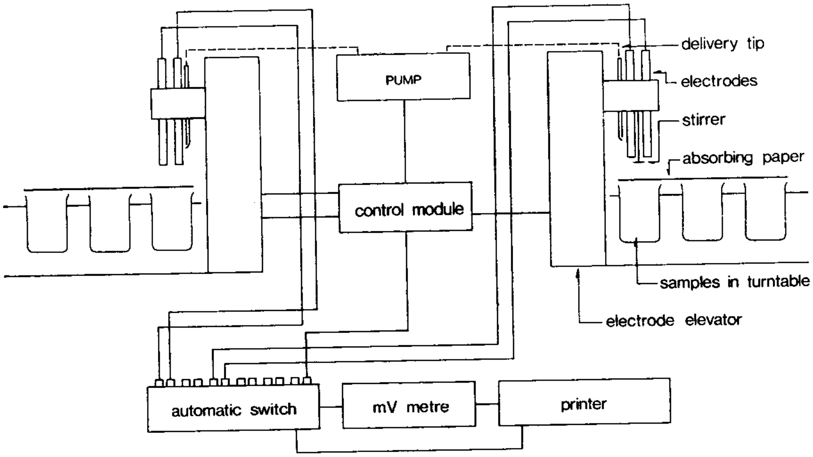


FIGURE 2 Block diagram of equipment assembly with two turntables.

The reading takes place at the end of the preselected time period. This time period can be 1, 6, 15, 30, or 60 min, and since six turntables can be incorporated and operated in one unit, sampling rates from 1 to 360 samples/hr are possible. However, a practical arrangement is two turntables. Taking the characteristics of ion-selective electrodes into consideration, a suitable sampling rate was found to be 20 samples/hr.

As the elevator lifts the electrodes, stirrer and delivery tip out of the sample beaker, the pump is momentarily activated to rinse down the electrodes and stirrer to remove carry-over droplets. The danger of the cross-contamination is suppressed primarily through rinsing and automatic "wiping" of the electrodes and the stirrer. The turntable rotates until the next beaker is in position, the cycle is repeated and automatically stopped after measurement of the final sample.

The determination of fluoride ion was conducted according to the method described by Orion Research Inc.[11] using total ionic strength adjustment buffer with CDTA. This method is based on previous publications.[12-14]. The ammonium ion was determined according to the Orion instruction manual for the ammonia electrode,[15] but instead of 0.1M NaOH, a 0.02M NaOH and 0.1M NaCl solution was used as the total ionic-strength adjusting buffer.

RESULTS AND DISCUSSION

The first question that arose was whether glass beakers could be used for the measurements of fluoride and ammonium ions, since there was a danger of ion losses due to the adsorption. In order to test this possibility, new 200-ml Berzelius beakers were washed with hot detergent solution, then with concentrated HNO_3, rinsed repeatedly with double-distilled water, and air-dried. Three samples of each test concentration (20, 100, and 200 mcg/l) of fluoride and ammonium ion were measured at intervals after an initial measurement at 1, 24, and 96 hr and compared to the measurements of freshly prepared standard solutions. The results are summarized in Table I and show no significant losses of the fluoride and ammonium ions.

The next test was focussed on the estimation of the time response for the electrodes to step-changes in concentration of the ion of interest. In other words, the estimation of the optimum time interval for the delayed measurements to obtain a correct reading by automated method, or the time required to change from baseline-steady state to sample-steady state and *vice versa.*

In order to achieve this, a series of samples of different concentrations was measured at 1, 3, 6, 10, and 30 min. The measurements were carried out at a gradual step-change from the lowest to the highest concentration by

TABLE I
Test of fluoride and ammonium ions adsorption on glass beakers

F^- added (mcg/l)	F^- found (mcg/l)			
	0 hr	1 hr	24 hr	96 hr
20	19	18	20	18
100	99	98	99	97
200	198	199	197	196
NH_4^+ added (mcg/l)	NH_4^+ found (mcg/l)			
20	19	18	17	19
100	98	98	97	97
200	197	201	198	199

continuously repeating measurements of the lowest concentration. The lowest concentration was 50 mcg/l and the order of the measurements was: 50–100–50–500–50–1,000–50–10,000–50–50,000–50 mcg/l of fluoride and ammonium ion, respectively. In this mode, increasingly larger step-changes of the concentration were introduced, reaching a maximum value of 1000-fold. The values of the electrode potentials after 30 min were assumed to be the correct values. This neglects the effect of random fluctuations about the

TABLE II
Time response of fluoride ion-selective electrode

F^- added (mcg/l)	Concentration change	% relative error[a]		
		1 min	3 min	6 min
50		+ 5.5	+ 1.5	+ 1.3
100	2×	−10.9	− 3.9	− 2.7
50		+11.1	+ 8.4	+ 1.8
500	10×	−12.2	− 7.6	− 1.4
50		+13.3	+ 5.8	+ 2.1
1000	20×	−12.0	− 6.4	− 1.7
50		+13.0	+ 4.7	+ 2.3
5000	100×	−10.0	− 3.3	− 1.8
50		+13.7	+ 4.2	+ 3.2
10,000	200×	− 6.5	− 2.9	− 1.4
50		+12.9	+ 5.9	+ 4.8
50,000	1000×	− 4.1	− 2.3	− 1.9
50		+23.3	+15.6	+12.3

[a] % relative error expressed relative to readings at 30 min, which were assumed to be correct.

TABLE III

Time response of ammonia ion-selective electrode

NH_4^+ added (mcg/l)	Concentration change	% relative error[a]		
		1 min	3 min	6 min
50		+18.4	+ 6.0	+ 2.2
100	2×	−19.2	− 5.8	− 2.8
50		+19.5	+ 7.2	+ 3.9
500	10×	−16.4	− 8.3	− 2.7
50		+20.8	+ 9.4	+ 3.5
1000	20×	− 7.7	− 6.1	− 2.8
50		+23.5	+ 8.7	+ 3.9
5000	100×	− 5.9	− 4.1	− 2.9
50		+27.9	+10.4	+ 5.5
10,000	200×	− 8.0	− 5.2	− 3.2
50		+31.5	+24.4	+12.8
50,000	1000×	− 6.7	− 5.2	− 3.0
50		+38.8	+27.2	+20.9

[a] % relative error expressed relative to readings at 30 min, which were assumed to be correct.

steady state reading. The readings obtained at other time intervals were compared with the readings obtained at the 30-min intervals and the differences were expressed as per cent relative error. The second aim of this test was to check for possible cross-contamination. The results of these tests, using the fluoride or ammonia electrodes, are given in Tables II and III, respectively. From these tables it follows that 1- and 3-min intervals are too short to allow the electrodes to reach the correct readings. The time interval

TABLE IV

Precision of the determination of fluoride and ammonium ions

F^- or NH_4^+ in the sample (mcg/l)	% rel. S.D.[a]	
	F^-	MH_4^+
20	3.9	4.8
50	1.8	2.8
100	1.6	2.2
500	1.6	1.9
1000	1.7	2.2
10,000	1.5	2.1

[a] n = 10 at each concentration.

TABLE V

Recovery of fluoride ion in synthetic lake water samples

Originally present (mcg/l)	Added (mcg/l)	Total (mcg/l)	Found (mcg/l)	Recovery (%)
50	100	150	146	97.5
50	500	550	540	98.1
100	100	200	203	101.5
100	500	600	591	98.3
500	500	1000	980	98.0
500	1000	1500	1530	102.0
1000	1000	2000	1950	97.5
1000	5000	6000	5900	98.3

of 6 min produced errors acceptable for the proposed system of automation of direct potentiometry. No significant cross-contamination was observed even in the case of a 1000-fold change in concentration.

The precision of the determinations of fluoride and ammonium ion was estimated through the measurement of 10 samples at each of the concentrations: 20, 50, 100, 500, 1000, and 10,000 mcg/l. The relative standard deviations were calculated and are summarized in Table IV. The values are in the range of 2% with the exception of the lowest concentration which was at the practical detection limits of the electrodes.

TABLE VI

Recovery of ammonium ion in lake water samples

Originally present (mcg/l)	Added (mcg/l)	Total (mcg/l)	Found (mcg/l)	Recovery (%)
15	100	115	110	95.5
15	200	215	220	102.6
18	200	218	210	96.2
23	5000	5023	5010	99.8
26	5000	5026	5050	100.4
33	200	233	220	94.1
44	5000	5044	5000	99.1
84	1000	1084	1100	101.5
100	1000	1100	1050	95.0
260	1000	1260	1300	103.2
680	2000	2680	2700	100.8
800	2000	2800	2900	103.6
1180	3000	4180	4000	95.5

Tables V and VI present the results of the determinations of fluoride and ammonium ion in water samples. Known amounts of fluoride ion in the concentration range from 50–1000 mcg/l were added to four samples of synthetic lake water. The solutions were then analyzed. After a second addition of fluoride ion, the analysis was repeated. The recovery of fluoride ion reached values from 97.5 to 102%. Thirteen samples of Lake Ontario water were analyzed for ammonium ion content; known amounts of ammonium ion were added, and the solutions were analyzed again. The recovery of ammonium ion was in the range of 9.4 to 10.4%.

A more detailed evaluation of the ammonia electrode in respect to routine analysis of ammonium ion in water samples will be presented at a later date. The fluoride electrode was chosen as an example of a well-known, verified, and commonly used ion-selective electrode for determination of fluoride in a variety of samples. The evaluation of this electrode can be found elsewhere.[11–14]

CONCLUSION

Automation of direct potentiometry, as presented in this study, overcomes some poblems of other automated systems and offers a wide range of possible applications for all types of ion-selective electrodes, including the glass electrode. The system is well suited for the specific requirements of ion-selective electrodes. The apparatus is relatively inexpensive, and simple to operate and maintain. There are no complicated operations involved when changing from one particular determination to another, or, in other words, the instrument is versatile enough for most applications of direct potentiometry.

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