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DETERMINATION OF INORGANIC ANIONS BY FLOW INJECTION ANALYSIS AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY COMBINED WITH PHOTOLYTIC-ELECTROCHEMICAL DETECTION

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SUMMARY

   Post-column, on-line photolytic derivatization in liquid chromatography with electrochemical detection for some inorganic anions is described. Flow injection analysis and ion-pair reversed-phase chromatography followed by photolysis and electrochemical detection were used for the determinations of anions. Several operation conditions, such as mobile phase, lamp used for the photolysis, flow-rate, and applied potential, have been optimized for the determinations. Analytical figures of merit were determined. Method validation was carried out by the analysis of single blind, spiked samples. Inherent from the advantages of electrochemical detection in liquid chromatography, the method is of high sensitivity and selectivity for anion analysis.

INTRODUCTION

   The powerful separation ability of high-performance liquid chromatography (HPLC) has been widely employed for the analysis of organic and biochemical mixtures. The availability of many chromatographic methods, based on the different models of separation, provides very sensitive and selective determination of many organic and biochemical species. The analysis of inorganic ions by HPLC, however, has not been as well developed. The reasons for this, in brief, may be two: (1) the poor retention of inorganic ions on the most commonly used reversed- and normal-phase columns; and (2) the poor detectability of most inorganic ions by the most commonly used ultraviolet (UV) (254 nm) and fluorescence (FL) detectors. Ion-exchange or ion-suppression chromatography (single or dual column), are the most commonly used methods for the analysis of ionizable compounds. Newly developed polymeric resins for ion chromatography column packings can be used within a wide range of pH and under high pressure with good reproducibility and high column efficiency. It provides a means for sensitive and selective determinations of inorganic ions. Another chromatographic method for ionizable compound separation is ion-pair chromatography[1]. Operated in the normal or reversed-phase modes, it also provides an efficient technique for the analysis of many ionogenic substances. With suitable detection

methods, ion-pair chromatography can be used easily for inorganic anion analysis. At present, the detection techniques available for inorganic anion analysis using ion-pair HPLC need to be improved.

Post-column, on-line, continuous photochemical irradiation has been shown to be an excellent derivatization approach for improved detection of many classes of organics by liquid chromatography–electrochemical detection (LC–ED)[2–8]. More recently, we have shown that a photoreduction process can occur in an aqueous methanol mobile phase, whereby nitrate can be efficiently converted into nitrite[9]. The nitrite was then detected at a variety of oxidative working potentials using thin layer amperometry with glassy carbon (GC) electrodes (dual parallel) to detect the original nitrate injected. Ion-pair chromatography was used together with photolytic-ED (hv-ED) in order to first separate nitrate from nitrite. It was clear that HPLC/flow injection analysis (FIA)–hv-ED could be immediately applicable to various inorganic, oxidized species, wherein these did not possess inherent oxidative ED properties.

This paper shows that it is possible to develop optimized HPLC and FIA–hv-ED analytical procedures to photoreduce and then sensitively detect inorganic anions under mild oxidative potentials with a GC electrode. It is likely that many other related inorganic species will prove suitable analytes for this basic analytical protocol. We describe in this paper the basic approach, instrumentation, optimized operational conditions, analytical figures of merit, and typical chromatograms using dual electrode detection. Qualitative and quantitative results will be presented for single blind, spiked sample determinations using ion-pair HPLC–hv-ED methods.

EXPERIMENTAL

Apparatus

The design of LC–hv-ED instrumentation has been described in detail[2]. Basically, the instrumentation consisted of an HPLC system, an irradiation apparatus, and an amperometric electrochemical detector. The HPLC system was composed of a Model 590 solvent delivery system (Waters, Milford, MA, U.S.A.), a LiChroma-Damp III pulse dampener (Handy and Harmon Tube Co., Norristown, PA, U.S.A.), a Rheodyne Model 7010 injector with a 20- or 50-μl sample loop (Rheodyne, Cotati, CA, U.S.A.), and a 10-μm LiChrospher C_{18} reversed-phase column (E. Merck, Darmstadt, F.R.G.). Mobile phase conditions will be given in the Discussion section. All mobile phases were filtered and degassed using a 0.45-μm solvent filtration kit (Millipore, Milford, MA, U.S.A.). Electrochemical detection was performed using dual amperometric controllers (Model LC-4B), a dual glassy carbon working electrode cell half operated at potentials of $+1.15$ V (all potentials were *vs.* Ag/AgCl reference electrode) and $+1.00$ V (dichromate and chromate ions, see figure captions for other anions) in parallel, a stainless-steel auxiliary electrode cell half, and a Ag/AgCl reference electrode (RE-1B), all obtained from Bioanalytical Systems (West Lafayette, IN, U.S.A.). The photolysis apparatus included a Photronix Model 816 UV batch irradiator (Photronix, Medway, MA, U.S.A.) with a quartz tube coil of 1.8 ml in volume. A zinc lamp (main irradiation line at 214 nm) and accompanying power supply obtained from BHK (Monrovia, CA, U.S.A.) were used as the UV light source for the irradiation of the samples. Also a photolytic reactor consisted of a knitted open tubular (KOT) reactor coil, constructed from 0.5 mm I.D. PTFE tubing (Rainin

Instruments, Woburn, MA, U.S.A.) and wound about a low pressure, mercury arc discharge lamp, was used for the photolysis of the analytes. The irradiation apparatus was maintained at 0–5°C using an ice–water bath. Upchurch fingertight fittings (Alltech Associates, Deerfield, IL, U.S.A.) were used to connect the column, irradiation unit, and electrochemical detector. The data were collected on an OmniScribe dual pen, strip chart recorder (Houston Instrument Co., Houston, TX, U.S.A.).

Chemicals, reagents and solvents

Inorganic standards were obtained in the highest available purity as follows: potassium dichromate, sodium thiocyanate and sodium perchlorate from Aldrich (Milwaukee, WI, U.S.A.), sodium chromate from J. T. Baker (Phillipsburg, NJ, U.S.A.), and potassium periodate from Fisher Scientific (Fairlawn, NJ, U.S.A.). Reagent grade sodium hydrogenphosphates (monobasic and dibasic) and sodium chloride were also obtained from Fisher Scientific. Ion-pair reagents, tetrabutyl-ammonium hydrogensulfate (TBAHS) and tetraethylammonium hydrogensulfate (TEAHS), were bought from Fluka (Ronkonkoma, NY, U.S.A.), and tetrabutyl-ammonium phosphate (TBAP) (IPC A) from Alltech Assoc. Methanol, the organic solvent used for preparing the mobile phase, was obtained from EM Science (Cherry Hill, NJ, U.S.A.) as their Omnisolv grade. Deionized water was prepared in our laboratory using a Barnstead water purification system (Sybron, Boston, MA, U.S.A.).

Procedures

Flow injection analysis (FIA)–photolysis (hv)-ED was carried out for the analytes before ion-pair HPLC–hv-ED was performed. Hydrodynamic voltammetry (HDV) was carried out using the FIA–hv-ED method. It was not necessary for this study to be carried out with an HPLC column on-line. The potential range for HDV studies was from +0.1 to +1.2 V. The hydrodynamic voltammograms were obtained in the conventional manner, by plotting ED response *vs.* applied potential.

The optimization of residence time of analytes in the photolytic reactor was performed by measuring the change in ED response with the change of flow-rate. The flow-rates used for this study were from 0.4 to 2.0 ml/min. The plot of peak height *vs.* flow-rate gave the optimal flow-rate condition for subsequent determinations.

The optimization of ion-pair HPLC–hv-ED detection involved the choice of proper mobile phase, including the ion-pair reagent, the electrolyte, pH and composition of the organic solvent in the mobile phase. Several mobile phases were tested for optimization of the mobile phase conditions. Details will be discussed below (Results and Discussion). Studies of linearity, reproducibility of the determinations, and determinations of spiked samples, were carried out under optimal mobile phase and flow-rate conditions using different concentrations of samples, all dissolved in the mobile phase. Calibration plots used for all quantitative determinations were obtained conventionally, by plotting peak height *vs.* concentration of samples.

RESULTS AND DISCUSSION

Determination for dichromate and chromate ions

Both dichromate and chromate ions are oxidized species which have no inherent oxidative ED properties. Direct ED after HPLC for these anions is difficult. However, it is known by photochemists that both anions have a photoreduction ability[10–14]. Although there is still some disagreement on the final photoreduction products, the photoderivatization of anions can be taken advantage of for the sensitive and selective detection of these anions combined with ion-pair reversed-phase chromatography. In Fig. 1, chromatograms are shown for dichromate ion, under both lamp on and lamp off conditions. When the lamp was off, there was no irradiation of the analyte, and the anion showed no ED response. However, it did show a sensitive ED response when the lamp was on. The same results were obtained for chromate ion. Since very little difference exists between the structures of dichromate and chromate ion, and in solution, both structures can be converted into hydrochromate ion, $HCrO_4^-$ (refs. 15
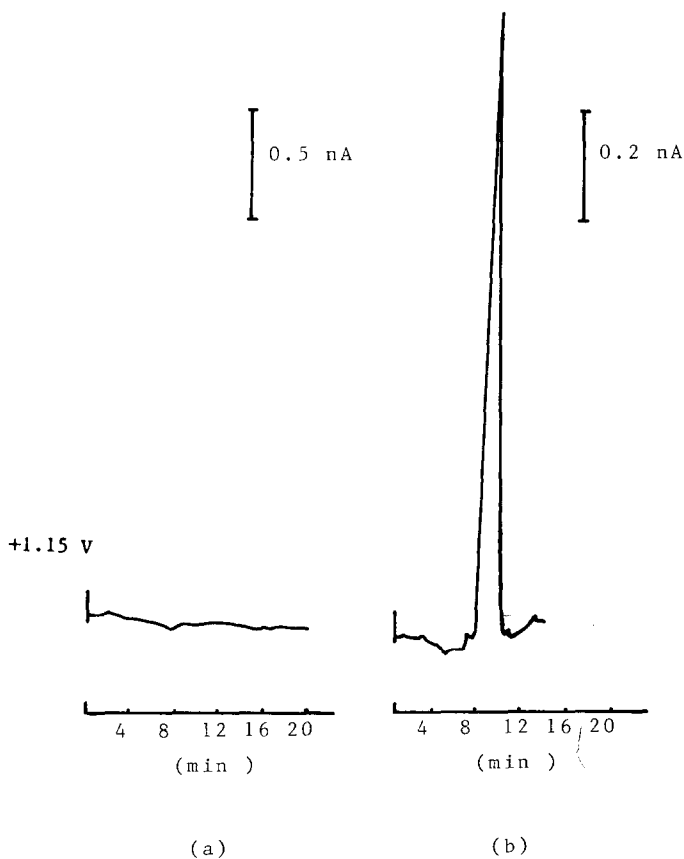

0.5 nA   0.2 nA

+1.15 V

| 4 | 8 | 12 | 16 | 20 |
(min)

| 4 | 8 | 12 | 16 | 20 |
(min)

(a)   (b)

Fig. 1. Ion-pair RPLC–hv-ED chromatograms of 20 ppm dichromate ion (potassium salt). (a) Lamp off; (b) lamp on. C_{18} reversed-phase column, 250 mm × 4.0 mm I.D., mobile phase, methanol–Na_2HPO_4 and NaH_2PO_4 (0.0070 and 0.0072 M) (30:70) (pH 6.8) with 0.0030 M TBAHS, flow-rate, 0.8 ml/min, injection volume, 50 μl. ED at +1.15 V, glassy carbon working electrode, Ag/AgCl reference electrode.

and 16), they were never separated chromatographically. There are apparently no literature reports of the HPLC separation of dichromate and chromate ions, under any conditions[17], perhaps due to the fast equilibria in solution. Thus, a quantitative determination of either species actually represented a combination of the mixtures, at least at a pH of 6.8. We have compared different pH conditions in FIA–hv-ED, and sensitivity of detection did not change greatly from pH 3.0 to 7.5, a range determined by the silica based RP column. This also indicated that FIA/HPLC–hv-ED methods for the detection of dichromate and chromate were actually the detection of total amounts of Cr^{6+} in solution.

Characterization of photolysis-ED for dichromate and chromate ions

    Initially, as part of the optimization for both anion's detection, hydrodynamic voltammetry (HDV) and the peak height change *vs.* flow-rate were performed using FIA–hv-ED. In Fig. 2, the HDV for potassium dichromate is shown. ED did not have a good response (lamp on) until the applied potential reached +0.6 V. A good linear relationship existed between ED response and applied potential between +0.6 and +1.15 V, suggesting that diffusion controlled ED was taking place. There were diffusion limited responses at $E_{app} \geq$ +1.20 V ($E_{1/2}$ = +0.91 V). The optimal potential for detection should be above +1.20 V. Considering the maximum possible potential of a GC working electrode (+1.25 V), working potentials for the determination of dichromate and chromate ions were chosen to be +1.15 V *vs.* Ag/AgCl. In Fig. 3, the plot of FIA–hv-ED responses *vs.* flow-rate for chromate is shown. Two factors can affect the final response under FIA/HPLC–hv-ED conditions when the flow-rate is changed. One is flow-rate itself, and another is residence time of the analyte in the irradiation tubing (photolytic reactor). According to the hydro-dynamic equations for laminar flow, an amperometric response is dependent on the cube root of the linear velocity of a flowing solution (without irradiation)[18], *i.e.*, the ED amperometric response should increase with the increase of flow-rate. However, as shown in Fig. 3, the lower flow-rates (longer residence times) gave much better
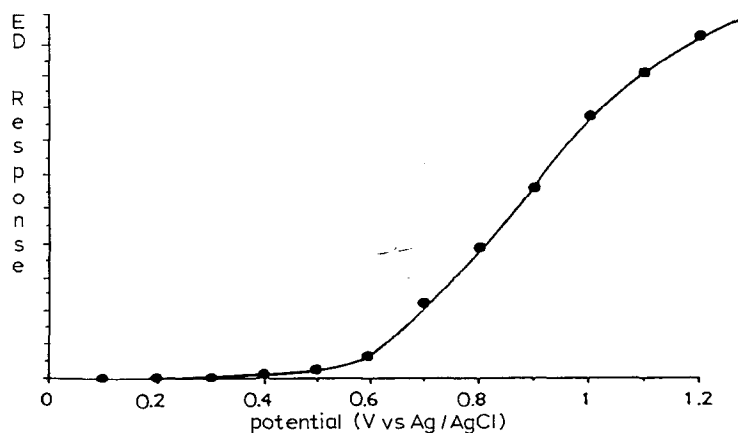

Fig. 2. Hydrodynamic voltammogram of irradiated dichromate ion (potassium salt) obtained using on-line photolysis with FIA–hv-ED. Mobile phase as in Fig. 1; flow-rate, 1.0 ml/min, injection volume, 50 μl. ED: glassy carbon working electrode, Ag/AgCl reference electrode.
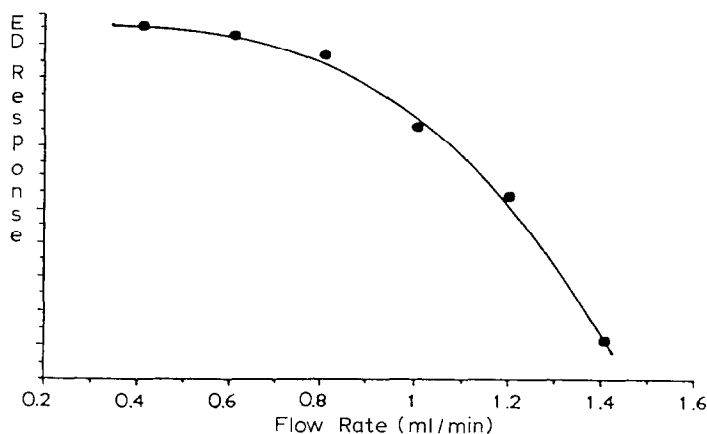
Fig. 3. Flow-rate optimization for the determination of chromate ion (sodium salt). C_{18} reversed-phase column, 250 mm $\times$ 4.0 mm I.D.; mobile phase as in Fig. 1; injection volume, 50 μl. ED, glassy carbon working electrode at $+1.15$ V, Ag/AgCl reference electrode.

responses. This simply indicated that the residence time of the anions in the irradiator played a more important role than flow-rate itself. However, at very low flow-rates (<0.7 ml/min), the peak broadening problem became more serious. From a practical point of view, a flow-rate of 0.7–1.0 ml/min was chosen.

Optimization of ion-pair HPLC–hv–ED

On-line, post-column photolysis-ED combined with ion-pair reversed-phase liquid chromatography for dichromate and chromate ions was initiated by using methanol–1 M NaCl (2:98, v/v) solution with TBAP ion-pair reagent (5 mM) as mobile phase. Later tetrabutylammonium hydrogensulfate (TBAHS) (5 mM) was used with the same methanol–NaCl solution instead of TBAP as ion-pair reagent. Finally, a Na_2HPO_4–NaH_2PO_4 buffer solution was used instead of NaCl as the electrolyte. The reason for changing the mobile phase was to reduce the background current so as to improve the sensitivity of detection. Commercial TBAP ion-pair reagent was found to have a large background current when used with hv-ED. Also, chloride ion contributed to the background current, especially at potentials $> +1.10$ V.

However, by using Na_2HPO_4–NaH_2PO_4 buffer (0.0070 and 0.0072 M) as the electrolyte and TBAHS (0.0030 M) as the ion-pair reagent, the background current was lowered to a few nA. Several mobile phases with different compositions of methanol–Na_2HPO_4 and NaH_2PO_4 buffer (10:90, 20:80, 30:70, v/v), all used with ion-pair reagent, were checked for the optimization of mobile phase conditions. Although mobile phases with 10 and 20% methanol gave longer retention times, the hv-ED response was significantly increased with a mobile phase containing 30% methanol. It seemed that methanol could help the photoreduction of dichromate or chromate ions or stabilize the photolytic products that were electrochemically active[12]. Finally, the optimal mobile phase for both ion-pair reversed-phase chromatographic retention and hv-ED was found to be methanol–Na_2HPO_4 and NaH_2PO_4 buffer (0.0070 and 0.0072 M) (30:70, v/v) (pH 6.8) with 0.0030 M TBAHS ion-pair reagent. All the following experiments were carried out using this optimal mobile phase.

Both the zinc lamp (with quartz coil) and mercury lamp [with a PTFE knitted open tubular (KOT) reactor] were used as light sources for the study of their effect on the photolytic responses. With the zinc lamp, maximum emission line at 214 nm, and a quartz coil used as the light source, under optimal mobile phase conditions, detection limits were in the sub-ppm range. However, signifiant band broadening resulted from the quartz coil (the zinc lamp can only be used with a quartz coil) and prevented any improvement of detection limits. However, there was no hv-ED response when the mercury lamp was used (with KOT). The energy of the main emission line of Hg (254 nm) was probably not high enough for dichromate ion to be photoreduced. Dichromate ion absorbs UV three times more strongly at 214 than at 254 nm, thus there is absorption at 254 nm, but the lower absorption and decreased intensity of irradiation may not be enough to promote photoreduction.

The linearity of the determinations for both dichromate and chromate ions are shown in Table I. A good linearity was observed within the working concentration range (2–100 ppm extended to detection limit, 0.5 ppm). The r^2 term was 0.9993 for dichromate and 0.9997 for chromate ion. The fact that relative standard deviations (R.S.D.s) (n = 3) for all data points were within 4% suggested that run-to-run reproducibility was excellent (dichromate standard as analyte). There is no comparison of slopes between dichromate and chromate ions due to the difference of absolute amount of total Cr^{6+} of the same concentrations of dichromate and chromate ions (in ppm) as well as the poor day-to-day reproducibility of the electrode surface.

In Table II, the mean, standard deviation (S.D.) and R.S.D. of three determinations are given for four single blind, spiked dichromate samples. Determinations were carried out by using a calibration curve. All determinations were performed in the same day as the calibration curve data were obtained. A comparison is made of the determined concentrations of dichromate samples with the actual spiked levels. The relative errors were within 5%.

Table III shows the three determinations, mean, S.D., and R.S.D. for four spiked chromate samples. The determinations shown were performed in 3 days with one determination per day. Each determination used a calibration curve obtained on

TABLE I

LINEARITY STUDY OF THE DETERMINATIONS

$Y = AX + B$, Y was the ED response and X was the concentration of the analyte in ppm. See Table V for linear response ranges. Chromatographic conditions: see Table II, Fig. 5 and text.

Analyte	Potential I[a]			Potential II[b]		
	A	B	r^2	A	B	r^2
Dichromate	0.993	3.339	0.9993	0.369	3.643	0.9971
Chromate	0.651	−0.241	0.9997	0.220	0.197	0.9995
Perchlorate	0.906	−1.025	0.9994	0.459	−2.211	0.9947
Thiocyanate	11.586	47.01	0.9973	1.833	12.109	0.9965

[a] Potential I for dichromate was +1.15 V, chromate +1.15 V, perchlorate +1.10 V, and thiocyanate +1.05 V.

[b] Potential II for dichromate was +1.00 V, chromate +1.00 V, perchlorate +0.90 V, and thiocyanate +0.90 V.

TABLE II

SUMMARY OF THE DETERMINATION OF CONCENTRATIONS OF SPIKED DICHROMATE SAMPLES[a]

Chromatographic conditions, C_{18} reversed-phase column, 250 mm × 4.0 mm I.D.; mobile phase, methanol–Na_2HPO_4 and NaH_2PO_4 (0.0070 and 0.0072 M) (30:70) with 0.003 M TBAHS; flow-rate, 0.8 ml/min; injection volume, 50 μl. ED, dual glassy carbon working electrode at +1.15 V and +1.00 V; Ag/AgCl reference electrode.

Spiked sample[b]	Determinations (ppm)			Mean (ppm)	S.D.	R.S.D. (%)
	I	II	III			
1	4.3	4.0	3.9	4.1	0.2	5.1
2	39.5	38.4	40.3	39.4	1.0	2.4
3	96.6	95.0	94.4	95.3	1.1	1.2
4	24.1	24.0	24.0	24.0	0.1	0.2

[a] At a potential of +1.15 V.
[b] Spiked in the mobile phase.

that day. Although these determinations were performed on different days, the R.S.D.s for these three determinations (four spiked samples) were less than 6%, and the relative errors between determined concentrations and actual spiked levels were within 4%. However, good agreement of the three different day's results did not mean good day-to-day reproducibility. Each determination used its own calibration curve, which was different from day-to-day. In fact, good agreement between different day's determinations was a direct result of good run-to-run reproducibility. The error was very small if both spiked sample determinations and calibration curve were obtained within a day. This is not surprising if we consider the fact, in general, of short term reproducibility for all ED, especially in flowing solutions.

In Table IV, the dual electrode response ratios are listed for both anions (obtained separately) with the S.D. and R.S.D. of measurements. The dual electrode response ratios for different sample concentrations were obtained by monitoring the samples at two different potentials (+1.15 V/+1.00 V) and taking the ratio of these

TABLE III

SUMMARY OF THE DETERMINATION OF CONCENTRATIONS OF SPIKED CHROMATE SAMPLES

At a potential of +1.15 V. Chromatographic conditions and ED as in Table II.

Spiked sample[a]	Determinations (ppm)			Mean (ppm)	S.D.	R.S.D. (%)
	I	II	III			
1	41.9	38.4	39.0	39.8	1.9	4.8
2	97.4	95.5	95.0	96.0	1.3	1.4
3	0.0	0.0	0.0	0.0	0.0	–
4	3.7	3.9	4.0	3.9	0.2	5.1

[a] Spiked in the mobile phase.

responses (peak heights). In general, there is good reproducibility of response ratios at all concentration levels. However, the response ratios changed slightly with the concentration change for both anions and also the response ratios for dichromate and chromate were a little different. The reason may again be the short term reproducibility of the electrode surface (these data were obtained on different days). In fact, we measured some of these response ratios again (only at some concentrations) on the same day, and found the same number for these ratios. This indicated that the dual electrode response ratio did not change with the concentration, and that they were the same for both dichromate and chromate ions, if the data were obtained on the same day.

Ion-pair HPLC–hν-ED for thiocyanate, perchlorate, and periodate ions

Besides dichromate and chromate ions, a number of inorganic anions have been evaluated for ED activity, with and without photolysis[19]. The results indicated that other anions, including perchlorate, periodate and thiocyanate, had oxidative responses photolytically induced, although they showed no ED responses under normal conditions (no irradiation). These anions were also evaluated for their detection using ion-pair HPLC–hν-ED. Perchlorate and periodate ions had no inherent ED responses because of their high oxidation states, but both were ED active after proper irradiation. In Fig. 4, the ED responses of periodate are shown with irradiation (lamp on) and without irradiation (lamp off). Thiocyanate ion had an ED signal with both lamp on and lamp off at higher applied potentials, i.e., $> +1.00$ V. However, improved detection sensitivity was obtained for this anion after irradiation. We have discussed other instances where organic compounds having native oxidative ED properties[6] showed improved detection sensitivity following irradiation.

FIA was used to optimize the applied potential and residence time of each analyte in the photoreactor. As shown in Fig. 5, the HDV of perchlorate ion indicated that a higher applied potential could give higher responses. However, the GC working electrode could only tolerate potentials less than $+1.25$ V. Meanwhile, the back-

TABLE IV

SUMMARY OF DUAL ELECTRODE RESPONSE RATIOS, i_1/i_2

Chromatographic conditions and ED as in Table II.

Concentration (ppm)	Dichromate ion[a]		Chromate ion[b]	
	i_1/i_2[c]	R.S.D. (%)	i_1/i_2[c]	R.S.D. (%)
0.5	—	—	2.00 ± 0.20	10.0
1.0	—	—	2.20 ± 0.26	11.6
5.0	1.87 ± 0.05	2.8	2.64 ± 0.06	2.2
10.0	1.96 ± 0.09	4.5	—	—
25.0	2.11 ± 0.04	2.0	2.60 ± 0.06	2.5
50.0	2.33 ± 0.01	0.3	2.78 ± 0.01	0.2
100.0	2.56 ± 0.03	1.0	2.96 ± 0.02	0.6

[a] As potassium dichromate.
[b] As sodium chromate.
[c] i_1 was the ED response at potential of $+1.15$ V, and i_2 was the ED response at potential of $+1.00$ V.
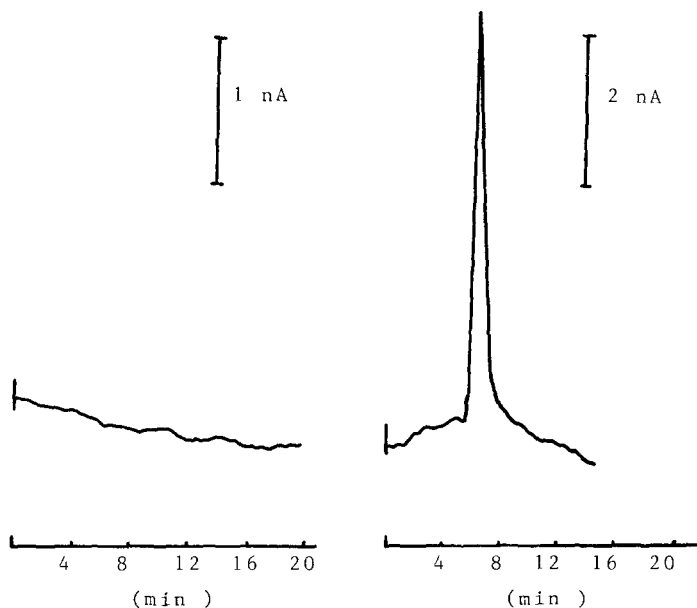
Fig. 4. Ion-pair RPLC–hν-ED chromatograms of periodate ion (potassium salt). (a) Lamp off, 40 ppm; (b) lamp on, 10 ppm; C_{18} reversed-phase column, 250 mm × 4.0 mm I.D.; mobile phase, methanol–Na_2HPO_4 and NaH_2PO_4 (0.0140 and 0.0144 M) (10:90) (pH 6.7) with 0.0060 M TBAHS; flow-rate, 0.8 ml/min; injection volume, 20 μl. ED at +1.00 V, glassy carbon working electrode, Ag/AgCl reference electrode.

ground currents at potentials higher than +1.15 V became too large. The final applied potential was selected as +1.10 V for perchlorate detection. For thiocyanate ion, the HDV was also obtained, and the final applied potential was selected as +1.05 V.

Flow-rate optimization was also carried out by FIA for these anions. The lower
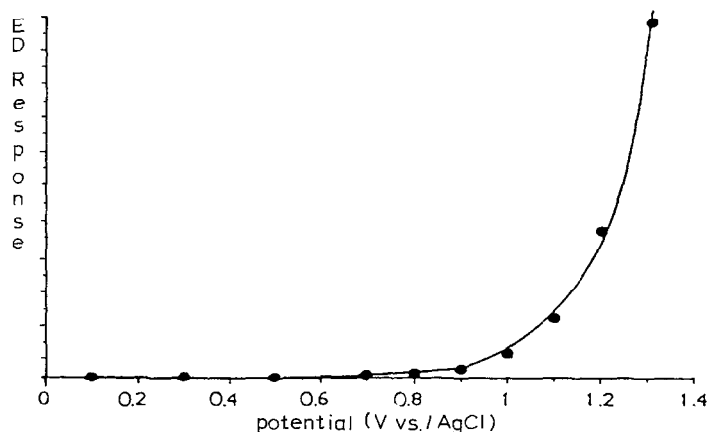
Fig. 5. Hydrodynamic voltammogram of irradiated perchlorate ion (sodium salt) obtained using on-line photolysis with FIA–hν-ED. Mobile phase, methanol–Na_2HPO_4 and NaH_2PO_4 (0.0070 and 0.0072 M) (20:80) (pH 6.8) with 0.0050 M TBAHS; flow-rate, 0.8 ml/min; injection volume, 20 μl. ED, glassy carbon working electrode, Ag/AgCl reference electrode.

the flow-rates, the larger the responses. As in the case of chromate/dichromate ions, too low flow-rates gave greatly broadened peaks. The optimal flow-rates were determined to be 0.7 and 0.8 ml/min for thiocyanate ion and perchlorate ion, respectively.

Both thiocyanate and perchlorate ions were well retained on the ion-pair RP-HPLC column with TBAHS. However, when tetraethylammonium hydrogen-sulfate (TEAHS) was used, both ions showed no retention even when the concentration of methanol in the mobile phase was as low as 2%. This was understood because of the shorter carbon chain of TEAHS. After trying several mobile phases (different methanol concentrations), the final mobile phase compositions for both ions were methanol–phosphate buffer (20:80) (thiocyanate) and methanol–phosphate buffer (18:82) (perchlorate). The separation of anions under study by ion-pair reversed-phase chromatography followed by photolysis-ED was carried out and the chromatograms obtained under both lamp on and lamp off are shown in Fig. 6. The mixture of periodate, perchlorate and thiocyanate could be well separated within 15 min. The ED
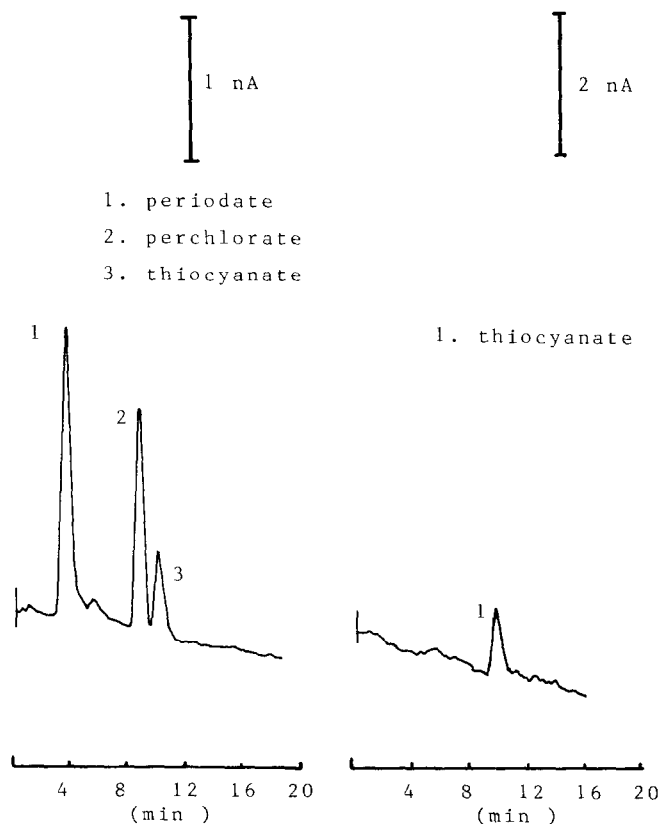
1 nA   2 nA

1. periodate
2. perchlorate
3. thiocyanate

1. thiocyanate

4   8   12   16   20   4   8   12   16   20
    (min)   (min)

Fig. 6. Ion-pair RPLC–hν-ED chromatograms of anions. (a) Lamp on; (b) lamp off. Sample concentration: 10 ppm periodate, 25 ppm perchlorate, 1 ppm thiocyanate. C_{18} reversed-phase column, 100 mm × 4.0 mm I.D.; mobile phase, methanol–Na_2HPO_4 and NaH_2PO_4 (0.0140 and 0.0144 M) (15:85) (pH 6.7) with 0.001 M TBAHS; flow-rate, 0.8 ml/min; injection volume, 20 μl. ED at +1.10 V, glassy carbon working electrode, Ag/AgCl reference electrode.

TABLE V

SUMMARY OF LINEARITY RANGES AND LIMITS OF DETECTION FOR INORGANIC ANIONS USING ION-PAIR RPLC–hv-ED

See Table II, Fig. 5 and text for chromatographic and ED conditions.

Anion	Limit of detection[a] (ppb)	Linearity range[b] (ppm)
Dichromate	300	100
Chromate	500	100
Perchlorate	300	200
Thiocyanate	70	200

[a] Obtained experimentally at signal-to-noise (S/N) equal to 3.
[b] Listed are only the maximum concentrations which were within the linear response ranges.

response differences between lamp on and lamp off offered another potential of selectivity in addition to the selectivity provided by the selection of working potential applied. For example, if another anion with inherent oxidative ED properties has the same retention time as perchlorate, the quantitative determination of this anion is possible under lamp off conditions, because there is no ED response for perchlorate. The peak obtained under lamp on conditions (containing two components) can be used to determine quantitatively the concentration of perchlorate (subtracting the peak area or peak height contributed from the first anion from the total peak area or peak height).

The linear response ranges for perchlorate and thiocyanate ions were measured, Table V, from the detection limits to 200 ppm. The data for the linearity study for these ions were given in Table I. The linear equation fitting the responses vs. concentrations gave r^2 values of 0.9973 and 0.9994 for thiocyanate and perchlorate. Detection limits (Table V) were 70 and 300 ppb (μg/l), respectively.

Periodate ion was not well retained on the RP column even with higher concentrations of ion-pair reagent. However, Fig. 4, periodate was very sensitive to hv-ED. 40 ppm potassium periodate was injected under lamp off conditions and nothing could be detected. On the other hand, 10 ppm of the same sample gave an off-scale response with the lamp on. The detection limit for this anion may also be several hundred ppb, though it was not physically determined.

ACKNOWLEDGEMENTS

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