

A Comparative Study of the Cylindrical Wire, Thin-Layer, and Wall-Jet Detector Cells for the Determination of Inorganic Arsenic by Ion Exclusion Chromatography with Constant and Pulsed Amperometric Detection

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ABSTRACT

An ion chromatographic method for the separation and determination of As(III) employing both constant and pulsed potential amperometric detection at platinum electrodes has been compared using cylindrical wire, thin layer, and wall-jet flow cell detectors. Operational parameters such as limit of detection, linear dynamic range, stability, reproducibility, and flow rate dependence are reported for each detector cell. The different detector designs have features which make them individually appealing, depending on the type of application being considered and which operational parameter is most important. However, the limit of detection with the wall-jet electrode of 1×10^{-9} M is superior to the other electrode designs (this may not necessarily be the case for other analytes) and makes this the preferred method for the determination of arsenic in bottled mineral water. Additionally, a lower limit of detection is achieved with constant potential amperometric detection than is the case with pulsed potential amperometric detection, which suggests that pulsed methods may not be advantageous for the detection of species at potentials where a large background current is exhibited at very positive potentials as required for the determination of arsenic.

KEY WORDS: Flow detectors, arsenic, ion chromatography.

INTRODUCTION

Flow-through electrochemical detectors are among the most popular detectors used in high performance liquid chromatography or flow-injection analysis because of their selectivity, high sensitivity, and linear response over a wide concentration range [1-13].

The majority of voltammetric detectors [1-10] described to date have employed liquid mercury electrodes or solid electrodes constructed from the noble metals and various forms of carbon. Solid electrode-

based detectors have been found to be easier to construct and simpler to operate than detectors employing a mercury electrode, and they have the ability to reach highly positive potentials unattainable with mercury electrodes. In addition, the unique surface properties of noble metals, in particular platinum, have been used advantageously to dramatically electrocatalyze a number of species [14, 15].

Among the most popular solid electrode flow cells used in voltammetry are those which have been based on the thin-layer, wall-jet and cylindrical wire designs [11, 16, 17]. The various designs differ essentially in the position of the working electrode relative to the direction of eluent flow; the thin-layer and cylindrical wire designs exhibit laminar flow parallel to the electrode surface,

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while the wall-jet design exhibits a flow direction perpendicular to the electrode surface. The majority of applications involving amperometric detection in flowing streams have used the thin-layer amperometric detector [18].

Comparative studies on the relative merits of individual flow cell designs generally have been confined to organic systems, in particular catecholamines [19, 20]. Several reports appear to indicate that the thin-layer design is more sensitive than other detector designs, despite the reduced mass transfer and higher uncompensated resistance through the flow cell [8,18]. It has also been argued in other studies that the wall-jet configuration is superior to other designs in terms of current sensitivity [21] and improved signal to noise ratio [22]. Equations describing the total electrode current generated at various flow cell geometries have been derived in terms of various cell parameters and have recently been tabulated [5, 6]. Comparisons between the actual performance and theoretical behavior of flow cell detectors have not proven to be entirely successful and significant differences have been observed. These differences have been attributed to specific effects of the electrode material, deviations in fluid flow, and inadequacies in the theory for the electrode current under certain operating conditions [7, 23].

The majority of applications employing LCEC have generally employed reverse- or normal-phase separations [24]. Recently, modern ion chromatography has been used with electrochemical detection to determine various inorganic and organic ions. The most common mode of separation is that of ion exchange chromatography which has been used to determine cyanide, sulfide, arsenite, phenols, aromatic amines, and numerous others [25–28]. Although conventional ion exchange techniques have normally been employed to separate a host of common anions, weakly acidic species such as As(III) are often poorly resolved [29]. Ion exclusion chromatography coupled with amperometric detection is a suitable method of differentiating between As(III) and As(V) with no interference from most other inorganic anions [30, 31].

In the present work, the performance of the thin-layer, wall-jet, and cylindrical wire flow cell detectors are compared for the anodic detection of arsenious acid ($\text{As}(\text{OH})_3$) using ion exclusion chromatography with constant potential and pulsed potential amperometry. The performance of the different flow cell detectors are evaluated and compared in terms of various operational parameters such as limit of detection, linear dynamic range, stability and reproducibility, and flow rate dependence. Pulsed potential amperometry was used to determine whether any improvement in the limit of detection or in the stability of the various flow cell detectors could be obtained by applying a sequence of potentials to the working electrode. The formation of a surface oxide at a platinum electrode is responsible for a large background current and plays an important role in the oxidation of As(III) to As(V). An earlier study [31] has demonstrated that with respect to limit of detection

and in many other respects that conventionally sized electrodes are superior to microelectrodes for the determination of As(III). Consequently, only conventionally sized electrodes were used in this comparative study.

EXPERIMENTAL

Reagents and Standard Solutions

Arsenic trioxide (As_2O_3) (BDH Chemicals) and phosphoric acid (H_3PO_4) (Ajax chemicals) were of Analytical Reagent-grade purity. Standard solutions of As(III) were prepared from As_2O_3 as described previously [31]. All working standards were prepared by serial dilution with either water or eluent (0.01M H_3PO_4) which was filtered through a Millipore (Type HA 0.45 μm) filter and degassed under vacuum in an ultrasonic bath prior to use.

Samples

Three mineral water samples were collected from local springs (Daylesford, Australia), acidified to pH 2 with sulphuric acid (Aristar grade, BDH Chemicals), and stored in precleaned polyethylene bottles at a temperature of 5°C prior to use. Three bottled mineral waters, one an Australian brand, and the other two imported from France, were also analyzed. All analytical determinations were performed within two weeks of collection of the samples since it has been reported that no appreciable oxidation of As(III) to As(V) occurs within this time [32]. As(III) was determined by direct injection of the mineral water sample, while total inorganic arsenic was measured after chemical reduction of As(V) to As(III) with sulfur dioxide. Details of the As(V) reduction method have been described previously [30, 31, 33].

Instrumentation

The chromatography system was constructed from individual components and is similar to the system used in an earlier study [31]. The majority of experiments were performed on a Waters Fast Fruit Juice column (polymeric base 10 μm , 150 mm length \times 7.8 mm diameter) with an eluent flow rate of 1.0 ml min⁻¹ although some experiments were also performed using a Brownlee Polypore H column (10 μm , 250 mm length \times 4.6 mm diameter) with an eluent flow rate of 0.6 ml min⁻¹. All chromatograms were recorded at 20°C using an injection volume of 200 μL .

The electrochemical system consisted of a BAS LC-4B Amperometric detector (Bioanalytical Systems Inc.) coupled to various flow cell designs which included the Metrohm 656 wall-jet (Metrohm, Herisau, Switzerland), a BAS thin-layer cube and external reference compartment (Bioanalytical Systems Inc.), and a cylindrical wire flow cell (Deakin University). The construction of the cylindrical wire flow cell is similar to that described elsewhere [17, 30]. The low pass filter con-

control on the LC-4B Amperometric detector was set at 1.0 Hz, except near the limit of detection, where the active filter was set at 0.1 Hz to reduce the noise. A Dionex Pulsed amperometric detector (Dionex Corporation) was used in place of the BAS LC-4B Amperometric detector for all experiments involving the application of more than one applied potential. To provide the lowest level of electronic noise, all detector cables were shielded and the entire LCEC system was connected to the same ground point.

Electrodes

The electrodes used with the thin-layer flow cell consisted of a platinum disk working electrode (area: 0.02 cm²) (Bioanalytical Systems), Ag/AgCl (RE-4) reference electrode and a platinum block auxiliary electrode. The Metrohm wall-jet flow cell contained a platinum disk working electrode (area: 0.02 cm²), Ag/AgCl (3M KCl) reference electrode and a platinum disk auxiliary electrode, while the cylindrical wire flow cell contained a platinum wire working electrode (area: 0.32 cm²) (21 mm length \times 0.5 mm diameter), Ag/AgCl (3M KCl) reference electrode and a platinum wire auxiliary electrode. Surface treatment of all working electrodes involved polishing with 0.5 μ m and 0.05 μ m alumina slurries, immersing in hot concentrated perchloric acid (HClO₄) and thoroughly rinsing with distilled water.

RESULTS AND DISCUSSION—CONSTANT POTENTIAL AMPEROMETRY

Constant potential amperometry is the most commonly used method of electrochemical detection for liquid chromatography [1]. A constant potential is applied continuously between the working and reference electrodes and the resulting oxidation or reduction currents are then measured between the working and auxiliary electrodes.

Detection of As(III) in a flowing stream is best suited to the use of the As(III) to As(V) oxidation process since the alternative use of the As(III) to As(0) reduction process is effected by the simultaneous reduction of dissolved oxygen [34, 35]. This oxidation process is used in the present work after separation from other species by ion chromatography (Figure 1).

Limit of Detection

The limit of detection (calculated as twice the standard deviation of the noise [44]) for each flow cell amperometric detector using a time constant of 1.0 and 10.0 seconds is shown in Table 1. Clearly, the use of a large time constant permits a much lower limit of detection to be obtained for all cell designs by minimizing the influence of high frequency noise without significantly affecting the amplitude of the analytical signal. The wall-jet and cylindrical wire amperometric detectors were found to have a lower

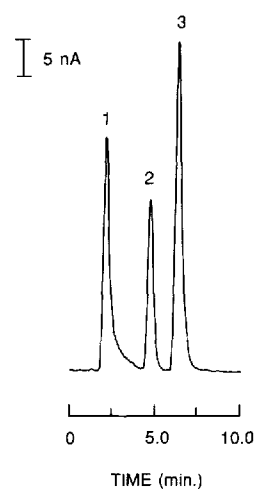


FIGURE 1. Separation of electroactive compounds by ion exclusion chromatography (Brownlee Polypore H column) with amperometric detection in a cylindrical wire flow cell: applied potential, 0.8 V vs. Ag/AgCl; flow rate: 0.6 ml min⁻¹; peak [1] oxalic acid, 50 μ M, [2] sulphite, 2.0 μ M, [3] As(III), 1 μ M.

detection limit for the determination of As(III) than the thin-layer amperometric detector. The increased surface area of the cylindrical wire electrode increases the conversion efficiency of the detector but does not improve the signal to noise ratio which essentially determines the limit of detection. A significantly larger noise component was observed with the thin-layer geometry when measuring low concentrations than with the other two designs. Although detection occurs in the thin-layer region, the larger separation of the reference electrode from the working and auxiliary electrodes must lead to larger uncompensated resistance through the flow cell. The wall-jet and cylindrical wire geometries differ in this respect from the thin-layer design, since all three electrodes are confined within the same cell body to minimize solution resistance. The lower uncompensated resistance could be responsible for the lower noise and lower RC time constant associated with these cell designs.

Linear Dynamic Range

The response index (r) of a detector can be used to measure the linearity of the concentration response and is defined by the following power function [36]

$$y = AC^r$$

where y is the detector output, C is the concentration, and A is a constant. The response index indicates the extent to which the detector performance deviates from ideal linearity ($r = 1$). Determinations based on peak height are normally made with reasonably high precision and accuracy, provided variations in such variables as column temperature, eluent flow rate, and rate of sample injection do not alter the peak widths

TABLE 1 Summary of Results Obtained At Various Flow Amperometric Detectors^a

Detector	Detection Limit ($\mu\text{g/l}$)	Linear Dynamic Concentration Range ($\mu\text{mol/l}$)	Response Index ^d (r)	Correlation Coefficient ^d	Response Index ^e (r)	Correlation Coefficient ^e	Flow Rate Dependence ^f (x)	Potential Range ^g V vs. Ag/AgCl
Wall-Jet ^h	0.40 ^b	0.10 ^c	0.01–50	0.99	0.99	0.98	1.00	+0.6 to +1.4
Cylindrical Wire ⁱ	0.80 ^b	0.45 ^c	0.01–50	0.98	0.99	0.98	1.00	+0.6 to +1.4
Thin Layer ^j	3.75 ^b	1.00 ^c	0.05–50	0.98	0.99	0.97	0.99	+0.6 to +1.4

^aApplied potential: 0.8 V vs. Ag/AgCl; flow rate: 1.0 ml min⁻¹; ^btime constant: 1.0 second; ^ctime constant: 10.0 seconds.

^dCalculations based on peak current ($y = AC^r$); ^eCalculations based on peak area ($y = AC^r$); ^f $i_L = knFCD^{2/3}U^x$;

^g accessible working range; ^hplatinum area: 0.02 cm²; ⁱplatinum area: 0.32 cm²; ^jplatinum area: 0.02 cm².

during the period required to perform the analysis. Analyses based on peak areas are essentially independent of broadening effects and are therefore considered a more satisfactory analytical parameter than peak height. In practice, peak heights are normally chosen since they are far more easily measured than areas, and for narrow peaks more accurately determined [37].

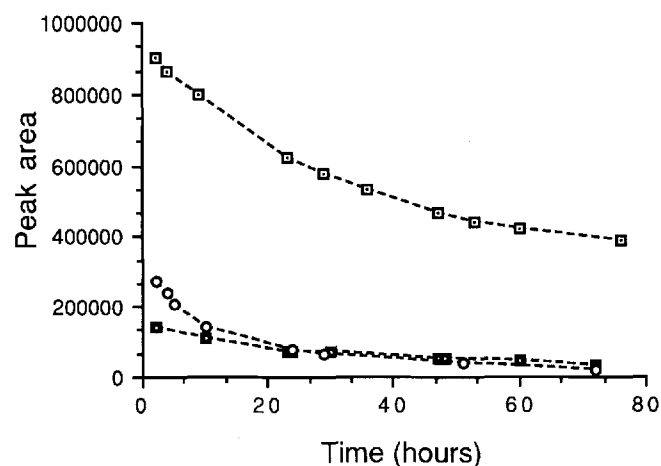
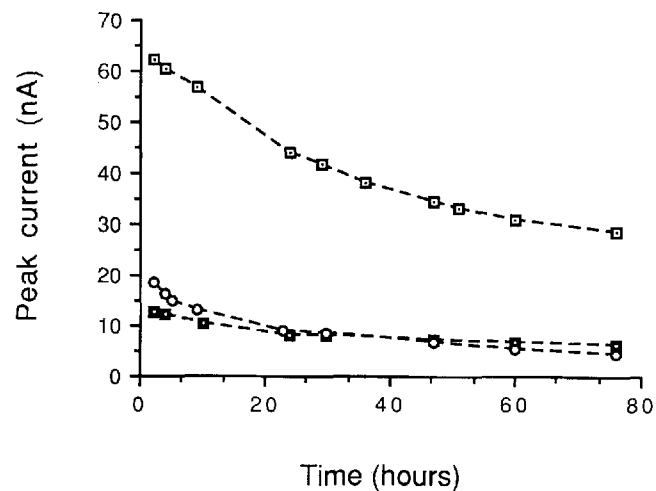
The response index and linear correlation coefficient of all three detectors in terms of peak current and peak area are summarized in Table 1. A linear dynamic range of all three flow cell detectors was found over the range of at least 0.01 μM to 50 μM As(III). Accurate measurements above 50 μM are limited by the maximum current measurable with the electronic circuitry, and are not accessible with the existing measuring system. Measurements of concentrations below 0.01 μM to the detection limit (Table 1) are probably linear but the signal-to-noise ratio causes some uncertainty in this low concentration range.

Stability and Reproducibility

The stability and reproducibility of solid electrode-based detectors has always been of considerable concern [5–10]. Platinum electrodes exhibit a substantial background response in aqueous media at very positive potentials. The background response is believed to be associated with the formation of a surface oxide in the form of adsorbed hydroxyl groups, which in turn play an important role in the oxidation of electroactive species such as As(III) [14, 15, 38, 39]. However, the longer term conversion to Pt-O has been reported to be responsible for some deterioration in the electrode response [38, 39].

The stability of all three detectors was evaluated by monitoring the decline in detector response for triplicate injections of 1 μM As(III) solution made over several days. The background current for each flow cell detector was allowed 2 hours to stabilize after the initial application of an applied potential of 0.8 V and the solvent delivery system was operated continuously at 1.0 ml min⁻¹. Figure 2 shows a comparison of the response decay exhibited by each flow cell detector in terms of the decline in peak current and peak area with

FIGURE 2. A comparison of the long term stability of the cylindrical wire (—□—), thin-layer (—○—) and wall-jet (—■—) amperometric detectors for the oxidation of 1 μM As(III): (a) decay in peak current with time and (b) decay in peak area with time; applied potential, 0.8 V vs. Ag/AgCl; flow rate, 1.0 ml min⁻¹.



time. All three flow cell geometries show a gradual loss in response over the first 24 hours before leveling off. However, this is generally not a problem when monitoring chromatograms since samples are readily compared with injections of standard solutions. While the electrode response for the wall-jet amperometric detector is somewhat smaller than the other detectors, it appears to stabilize appreciably faster than the cylindrical wire and thin-layer designs.

Reactivation of the electrode surface was achieved by mechanically polishing the electrode with alumina, immersing in hot concentrated perchloric acid, and rinsing thoroughly with distilled water. This procedure ensured the removal of any foreign material from the electrode surface as well as maintaining a clean surface with which reliable measurements could be made. Polarizing the electrode surface at an applied potential of 1.2 V vs. Ag/AgCl and then re-equilibrating the electrode at its detection potential did not improve reproducibility, although it did temporarily enhance the response for the cylindrical wire detector. No improvement in re-reproducibility or enhanced current was observed with the wall-jet or thin-layer designs.

Flow Rate Dependence

An unfortunate feature associated with flow voltammetric detectors is that they generally exhibit a flow rate dependence. Figure 3 shows the effect of flow rate on the detector response for the various flow cells immediately after the background current is allowed to stabilize. The flow rate dependence can be quantified by considering the general equation [13, 40]

$$i_L = knFD^{2/3}U^x \quad (1)$$

where i_L is the limiting current of a hydrodynamic voltammogram, k is the constant kinetic viscosity coefficient depending on the area of electrode, n is the number of electrons transferred, F the Faraday constant, C the concentration of a sample, D the diffusion coefficient, U the flow rate and x the exponential coefficient depending on the structure of the electrode. The logarithm of i_L is given by the following equation:

$$\log i_L = \log K + x \log U \quad (2)$$

where $K = knFD^{2/3}C$. The value of x which is a characteristic of each detector can now be determined from the slope of the graph of $\log i_L$ against $\log U$. Values of x obtained from the peak height measurement versus $\log U$ for each detector are reported in Table 1 under conditions relevant to Figure 3. Given that the peak height rather than i_L was used and that this is an electrode process where the state of the electrode surface is important, then it is very difficult [23] to compare the result with theory [13, 40, 41]. However, it is apparent that a significant dependence on flow rate is observed for all detectors, and at no stage during the experiment was flow rate independent data obtained at any of the detector designs despite the tendency for the peak current to become less dependent on flow rate with time. The value of x is generally found to be one

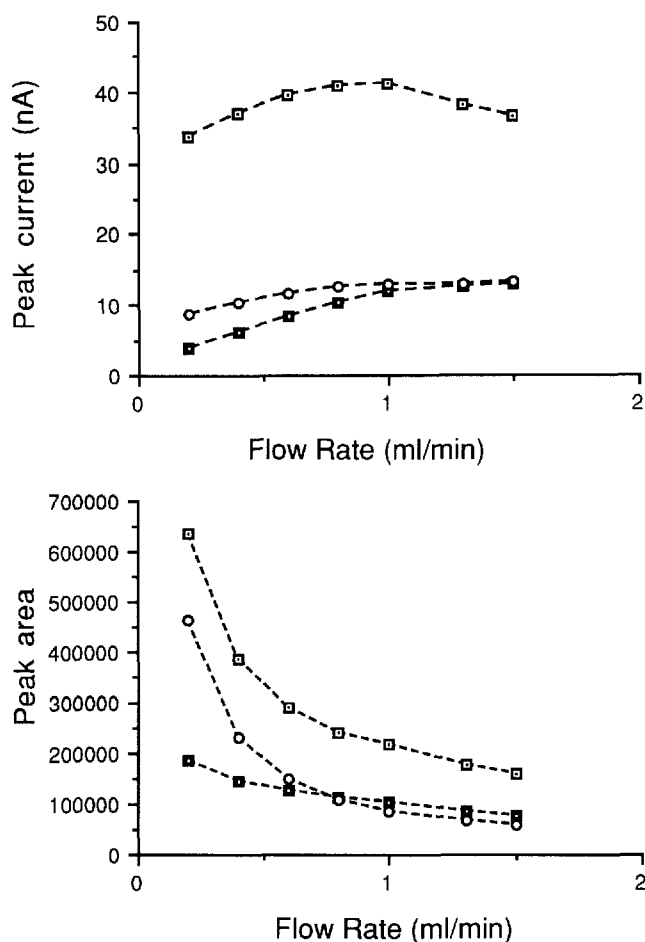


FIGURE 3. Dependence of flow rate on detector response for the oxidation of $1 \mu\text{M As(III)}$ at a cylindrical wire (\square), thin layer (\circ) and wall jet (\blacksquare) amperometric detector: (a) plot of peak current versus flow rate and (b) plot of peak area versus flow rate; applied potential, 0.8 V vs. Ag/AgCl.

third for a cylindrical and thin-layer electrode (although a half also has been frequently reported) and three quarters for a wall-jet electrode [41]. The detector response clearly depends on the concentration of the sample (C) and the flow rate (U) and values of x for each detector are reported in Table 1. All three detectors exhibit a smaller flow rate dependence than predicted by theory, although reasonable agreement is observed with the wall-jet and thin-layer designs.

Flow Cell Characteristics

All three flow cell designs have particular characteristics which make them individually appealing for use in LCEC. The thin-layer and cylindrical wire designs have a relatively fixed working electrode resulting in a constant cell volume. In contrast, the position of the working electrode in the wall-jet detector can be easily altered enabling the cell volume to be varied. This can present a problem, since the position of the working electrode

can cause a variation in the performance of the wall-jet flow cell. Optimum performance was obtained with the wall-jet configuration when the working electrode was relatively close to the impinging jet, and a loss in performance was observed as the electrode was positioned further away from the orifice of the jet.

The fluorocarbon gasket between the working and auxiliary electrodes in the thin-layer cell was found to affect the magnitude of the analytical signal, but no improvement in the signal to noise ratio was observed. Decreasing the spacer thickness (100 μm –50 μm) increased the analytical response but also increased the amount of baseline noise, while increasing the spacer thickness (50 μm –100 μm) decreased the amount of baseline noise, but at the same time decreased the analytical response.

The larger surface area of the cylindrical wire electrode enables a much larger analytical response to be obtained. Unfortunately, a larger background current is also present, and consequently the detector requires more time to stabilize. Maintenance of the cylindrical wire electrode is far more difficult than with the thin-layer and wall-jet configurations since the cell cannot be readily disassembled making access to the working electrode difficult.

PULSE POTENTIAL AMPEROMETRY

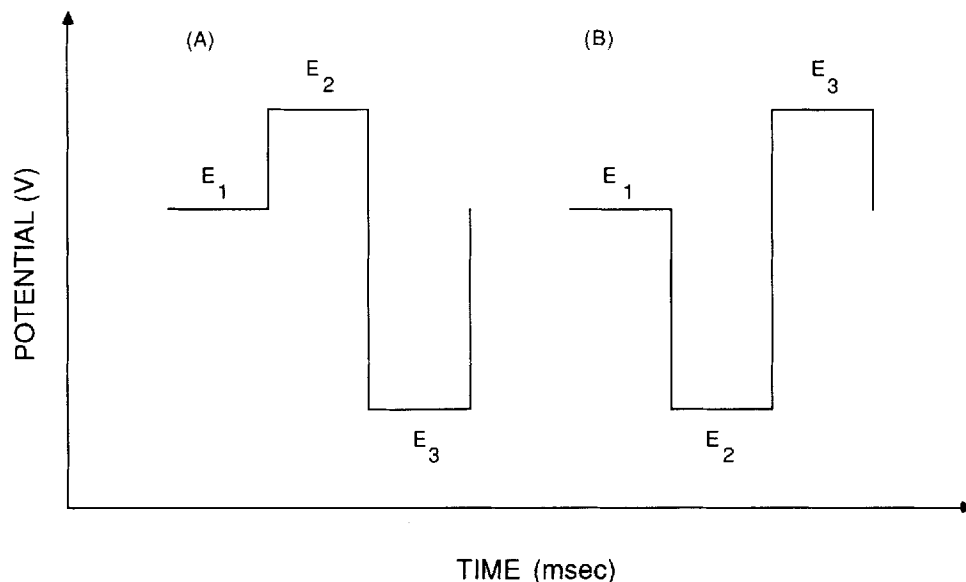
The loss of activity at noble metal electrodes such as Pt under flowing conditions has been of considerable concern to electroanalytical chemists [43, 44]. The decay in electrode response is usually attributed to gradual fouling of the surface due to adsorption, film formation, and other related phenomena. Maintaining a reliable and reproducible surface can often be difficult, and while mechanical polishing normally restores the electrode to its full current response, it is often time consuming and an inconvenience.

Recently, cleaning pulses [14] have been used with

some success to eliminate passivation of the electrode by the use of a pulsed waveform which incorporates a potential capable of cleaning the surface of an electrode. Pulsed amperometric detection (PAD) has been used successfully in numerous applications to effectively remove reaction products or interfering species from the electrode surface. The method essentially involves applying a sequence of repeating potentials to the working electrode which effectively cleans the surface of any adsorbed species which may cause electrode fouling. The technique has proven to be particularly useful for determining organic compounds which are adsorbed by noble metal electrodes such as platinum and which are not readily detected using a constant electrode potential. Detection with PAD at platinum electrodes has been used successfully for analysis of carbohydrates, amino acids, alcohols, amines, and arsenite [14, 45–50] in alkaline solutions. This eluent has been reported as the most suitable for PAD [48].

In an effort to determine whether any improvement in the stability or limit of detection of arsenic could be obtained by using PAD under aqueous acidic conditions, various positive and negative pulses were applied to the working electrode by a Dionex pulsed amperometric detector coupled to the various flow cell designs. Triple step potential waveforms [14] of the type A and B shown in Figure 4 were then applied at different time intervals and the current sampled at the end of the detection period (T_1) at potential (E_1). The selection of a suitable waveform can be a complicated task since there are essentially six parameters: E_1 , E_2 , E_3 (pulse potentials) and T_1 , T_2 , T_3 (pulse durations) which need to be addressed. Initial studies were carried out using a single potential at the wall-jet flow cell, since the background current is much lower than for the thin layer and cylindrical wire flow cells. The detection potential (E_1) was chosen to correspond with the rapid formation of the surface oxide (Pt-OH) on the detector

FIGURE 4. Triple step potential waveforms used in pulsed amperometric detection.



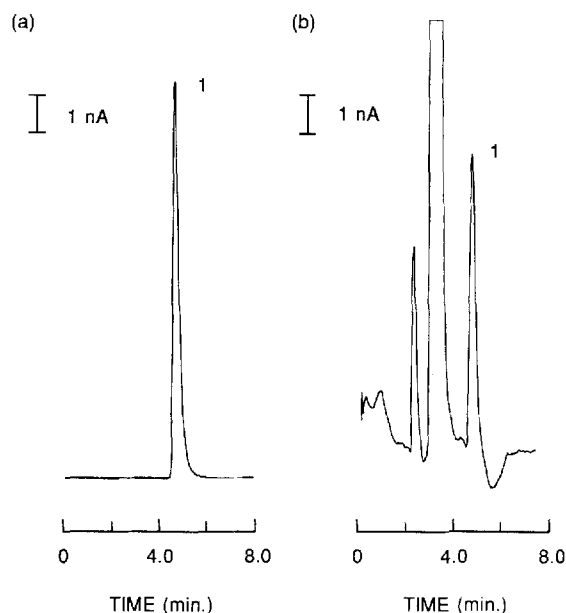


FIGURE 5. Ion chromatograms (Waters Fast Fruit Juice column) for the oxidation of $1 \mu\text{M}$ As(III) at a wall-jet amperometric detector using (a) a constant electrode potential ($E_1 = 0.8\text{V}$) and (b) a triple-step potential waveform ($E_1 = 0.8\text{ V}$, $E_2 = 1.35\text{ V}$, $E_3 = 0.3\text{ V}$): flow rate, 1.0 ml min^{-1} .

electrode while optimum values for E_2 and E_3 were determined by trial and error.

No improvement in detector response was observed relative to the constant potential detection method, regardless of which type of waveform A or B (Figure 4) was applied or whether two or three pulse potentials were chosen. The level of background noise with all detector cells was found to increase significantly, and the baseline signal steadily drifted making measurements difficult. Figure 5 shows a comparison of the ion chromatograms obtained using a constant electrode potential ($E_1 = 0.8\text{ V}$) and a triple-step potential waveform (anodic detection ($E_1 = 0.8\text{ V}$), anodic cleaning ($E_2 = 1.35\text{ V}$) and cathodic reactivation ($E_3 = 0.3\text{ V}$)) at a wall jet flow cell. Each pulse duration was set at 60 mSec and the peak current sampled near the end of E_1 for 20 mSec to cancel 50 Hz noise. Similar behavior was observed for the thin layer and cylindrical wire detectors.

The application of a sequence of repeated pulses generates two additional peaks as well as the peak due to the oxidation of As(III). These peaks arise from the mobile phase solvent since they are also detected for injection of the eluent without As(III) being present.

The stability of the wall-jet pulsed amperometric detector using the potential sequence above was compared with the wall-jet amperometric detector operated at a detector potential of 0.8 volts. Figure 6 shows a comparison between the response decay using a constant electrode potential and a triple step potential waveform at the wall-jet flow cell. Although the use of

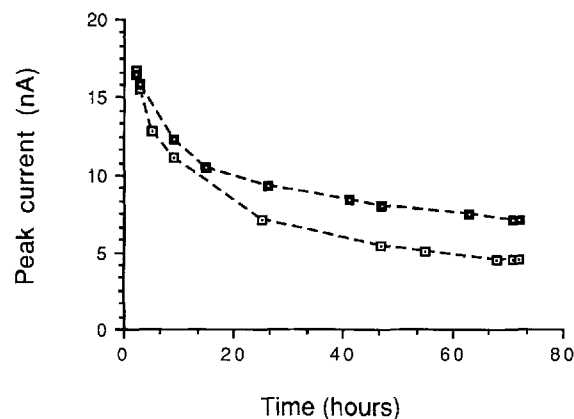


FIGURE 6. A comparison of the long term stability for detection of $1\mu\text{M}$ As(III) at a wall jet amperometric detector using a constant electrode potential ($E_1 = 0.8\text{ V}$) (\square) and a triple step potential waveform ($E_1 = 0.8\text{ V}$, $E_2 = 1.35\text{ V}$, $E_3 = 0.3\text{ V}$) (\blacksquare): flow rate, 1.0 ml min^{-1} .

PAD at a Pt electrode improves the stability of the detector, there is still a visible loss of activity at the electrode surface. A significant increase in electronic noise was observed with the Dionex PAD when a triple step potential waveform was applied, although the analytical response was found to be similar. The baseline noise increase may be due in part to the sample and hold circuitry associated with the PAD.

The substantial background current caused by the formation of a surface oxide at the Pt electrode requires a significant time to stabilize as the applied potential is changed. The amount of low frequency noise restricts the usefulness of pulsed amperometric detection as a highly sensitive analytical technique in acidic media. No advantage was obtained by using PAD over a single potential under the conditions stated herein. Previous work with PAD has been performed in alkaline media, which has been suggested to be a requirement for successful application of PAD [48]. From our current findings, it would appear that PAD may not be advantageous for detection of species which exhibit a large background current under acidic conditions.

Determination of Inorganic Arsenic in Mineral Water by LCEC

The level of arsenic in mineral water is generally very low. Consequently, the most sensitive method available in this work, which is the wall-jet amperometric detector, was used to ascertain whether inorganic arsenic could be determined in a range of mineral water samples. Of the six mineral water samples examined for inorganic arsenic (see Experimental Section), two were found to contain a measurable amount of As(V) after reduction with SO_2 (see experimental), while a third mineral water sample was found to contain As(V) at a level corresponding to the minimum detectable concentration. The arsenic concentrations in the remaining samples were too low to be determined and are assumed to be

TABLE 2 Determination of Arsenic in Mineral Water Samples^a

Sample	Arsenic(III) Found ($\mu\text{g/l}$)	Total Inorganic Arsenic Found ($\mu\text{g/l}$)
Mount Franklin (Australia) ^b	ND ^c	1.0 ± 0.5
Volvic (France) ^b	ND ^c	14.9 ± 0.6
Ballan Mineral Spring (Australia)	ND ^c	<0.4 ^d

^aWall jet amperometric detector. Applied potential: 0.8 V vs. Ag/AgCl, Flow rate: 1.0 ml min⁻¹. ^bCommercially available bottled mineral water.
^cND — not detected.
^dArsenic concentration is at minimum detectable concentration of 0.4 $\mu\text{g/l}$ where signal to noise ratio is 2:1. Other three samples examined are therefore assumed to have values $< 0.4 \mu\text{g/l}$.

$< 0.4 \mu\text{l}$. Results are summarized in Table 2. The fact that As(III) could not be detected in any of the mineral water samples is consistent to previous reports that As(V) is the most common environmental form of arsenic [42]. The total arsenic concentration was determined by using the method of standard additions with individual data points being the average of three determinations. The determination of arsenic in mineral water is an example, where the wall-jet detector must be used in preference to the cylindrical wire or thin layer designs because only this detector has adequate sensitivity.

CONCLUSION

An ion chromatographic method for the separation and detection of As(III) based on electrochemical detection has been used to compare the performance of the thin-layer, cylindrical wire and wall-jet flow cell detectors designs in terms of various operational parameters. All three designs exhibit properties which make them individually appealing depending on the type of application required. In the present work, a detection limit of 0.10 ppb ($1 \times 10^{-9}\text{M}$) was obtained at the wall-jet amperometric detector using a large time constant of 10.0 seconds. All three detector flow cells exhibit a wide linear range, a smaller flow rate dependence than predicted by theory, and a gradual loss of activity with long term use. The use of pulsed amperometric detection did not improve the stability or limit of detection of As(III).

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