Development of an in-field method for the detection of barium in various water samples using differential pulse anodic stripping voltammetry

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This work presents a reliable, cost-effective, rapid and in-field voltammetric method for the detection of barium. The optimized method consists of an ultrathin mercury film deposited in situ on a glassy carbon electrode in dilute potassium chloride without deoxygenation, using differential pulse anodic stripping voltammetry (DP-ASV). Application of the method allowed for the quantitative determination of barium concentration in a variety of waters and brake pad dust samples. Comparative analysis of sample results from DP-ASV with inductively coupled plasma mass spectroscopy (ICP-MS) showed a mean percent difference of 1.8%.

1. Introduction

The pervasive use of barium compounds in our society has led to interest in the effects of accumulation of barium compounds in the environment [1]. Although few published studies exist, negative effects of dissolved barium on aquatic life in marine waters have been reported, specifically for bivalves and daphnids [1], important indicator species for monitoring water quality. Environmental management concerns have been raised in the UK and USA about long-term accumulation of barium in river sediments and groundwater [2, 3]. In a review by Kravchenko et al. [3], the authors further note that recent expansion of shale gas drilling has heightened the risk of barium pollution in groundwater and wells, igniting scientific interest for investigation of potential human and environmental health impacts, due to the dearth of published information.

The sources of drinking water contamination are usually from the erosion of natural deposits, discharge of drilling wastes, and discharge from metal refineries [3]. In 2011 the World Health Organisation (WHO) revised its global drinking water guideline for barium from 2 mg/L down to 0.7 mg/L [4]. The US Environmental Protection Agency (EPA) and Australian drinking water guidelines remain at 2 mg/L [5, 6], despite studies reporting that chronic exposure to barium at low concentrations may be problematic [3]. Also, recent studies conducted in Bangladesh and Vietnam strongly suggest that the presence of barium promotes the carcinogenicity of arsenic in tube-wells [7, 8]. In addition, brake dust has recently been shown to be a major contributor of particulate matter in urban air pollution following studies conducted in the UK [9]. Barite is a filler material in brake pads and has been defined as a unique tracer to differentiate brake wear pollution from the wear of other car parts [10].

Routine analysis of heavy metals can be performed by a suite of analytical chemical methods; however, inductively coupled plasma mass spectrometry (ICP-MS) and flame atomic absorption spectrometry (FAAS) are the most commonly applied techniques because they are well established accredited methods [5, 6]. Laboratory analyses using these methods are expensive, can be time-consuming, and are not suitable for in-field analysis. An in situ and inexpensive portable analytical method would be an attractive alternative in remote locations or when immediate and on-site results are a necessity [11].

Voltammetry could provide such an alternative technique. Voltameters are easily available, portable, and relatively cheap compared with ICP-MS and FAAS, and anodic
stripping voltammetry (ASV) is one of several officially recognized techniques for the detection and speciation of metal ions in natural waters outlined in the Australian National Water Quality Management Strategy [6].

Difficulties pertaining to barium analysis by ASV have been reported by most researchers, particularly in connection with gunshot residue analysis [12–14], and are related to barium’s highly negative standard reduction potential [15]. Use of highly negative deposition potentials in voltammetry result in the evolution of gases at the working electrode that interfere with the barium signal [16]. This study, therefore, has predominantly focused on the fundamental development of an in-field ASV method for the detection of barium at the least negative deposition potential for the shortest amount of time to mitigate the problem. The secondary focus of this project, therefore, was the potential application of the developed ASV method to detection of barium in several types of samples, such as drinking water and brake pad dust.

2. Experimental

2.1. Reagents. All metal standards purchased were ICP grade from Australian Chemical Reagents (ACR). 1000 mg/L metal standards in 2% nitric acid solution were obtained from ACR for mercury and barium. Analytical grade potassium chloride ≥99.9995% (Fluka) was purchased from Sigma-Aldrich (Sydney, Australia). Nitric acid 69% Suprapur® was purchased from Merck (Australia). All solutions were prepared with deionized water generated by a Millipore Milli-Q water system (Bedford Massachusetts, USA) with resistivity not less than 18.2 MΩ cm−1 at 25 °C. Certified GhostWipes™ Standards of 100 μg barium per wipe were purchased from EnviroExpress.

2.2. Apparatus. All measurements were conducted on a Modern Water PDV6000plus instrument (portable, digital voltmeter) equipped with a 3-electrode cell and plastic analysis vessel. The working electrodes were manufactured at B3 Electronics, Osborne Park Western Australia. These electrodes were glassy carbon, solid gold, and solid bismuth (surface area of 5 mm²). The reference electrode was Ag/AgCl/1.0 M KCl and the auxiliary electrode was a platinum wire coil. An IBM Thinkpad laptop (Model number 23736YM) was used in connection with the PDV6000plus potentiostat and controlled via Voltammetric Analysis Software (VAS) version 5.1 to generate voltammograms.

ICP-MS analysis was performed at ChemCentre, WA, on all samples. The metal Ba was analysed by ICP-MS method iMET1WCM5 (APHA 3125) and calcium (Ca) was analysed by ICP-AES method iMET1WCIC5 (APHA 3120). Lines used were Ba 455.403 nm, Ba 233.527 nm, and confirmation line Ba 493.408 nm.

All method development results were expressed as mean values and calculated using Excel for Mac 2011, Version 14.0.0. Sample results were calculated using VAS 5.1 linear regression analysis. Comparative analysis between ASV and ICP-MS was performed using IBM SPSS Statistics.

2.3. Sample Analysis

2.3.1. Sample Collection and Preparation. Various types of drinking water samples were collected at locations in the Northern Metropolitan area and surrounds of Perth, Western Australia. These were tap water, bore water, bottled water, and a sample from a rainwater tank. Samples were collected in 1 L plastic bottles that were triple rinsed prior to filling. Bore water samples were collected by the property owners in Muchea, Bullsbrook, Craigie, and Wangara, WA. Bottled water was purchased at a local supermarket and remained sealed until analysis. Tap water was collected from the author’s home kitchen faucet in Wanneroo, a drinking water fountain on the Joondalup campus at Edith Cowan University, and from a church in Bullsbrook where the patrons freely drink the supplied ‘holy water’, obtained from a faucet on the grounds.

2.3.2. Brake Pad Dust. Vehicle wheel rims, brake calipers, and brake pads were wiped with cotton cleaning patches or Ghostwipes™ in accordance with NIOSH (2009) procedures and placed in 50 mL sample tubes. Brake pads covered in loose dust were shaken into 50 mL sample tubes for dust particle collection. All samples were submerged in 15.0 mL 3% HNO₃ solution to undergo extraction for 24 hours and sent for ICP-MS analysis.

2.3.3. Sample Preparation. Water samples were diluted prior to voltammetric analyses. Samples were run as 2 mL aliquots, in 18 mL 0.02 M KCl electrolyte with a 100 μL aliquot of 1000 mg/L Hg standard in the 20 mL analysis cup. These quantities provided the electrolyte conditions of 0.02 M KCl and 5 mg/L Hg in the optimized method and not more than 1.5 mM HNO₃ content.

For voltammetric analysis, brake pad dust samples were diluted to 63 μL aliquot of sample added to 19.37 mL of 0.02 M KCl with 5 mg/L of Hg electrolyte solution, equal to 3.0 mM total content of HNO₃. For ICP-MS analysis, 9 mL aliquots of sample plus 1 mL 3% nitric acid were transferred to 15 mL sample tubes and sealed.

3. Results and Discussion

3.1. Method Development. The development of the method for barium analysis, involved testing various electrodes and defining the optimum voltammetric parameters, and then once the most promising system was established investigating more thoroughly, validating the method by determining linear working range, limit of detection, and stability.

Following optimization, the method was then applied to a variety of samples and the results were compared to ICP-MS analysis.

3.1.1. Electrode Investigation. In the development of an ASV method for barium detection, one of the key factors was the choice of electrode. Glassy carbon (GCE) has been the most commonly employed electrode in combination with linear sweep or differential pulse mode for potential delivery [12, 14, 17]. Consequently, the GCE system was used as a
starting point for the determination of key voltammetric parameters, which are crucial for the successful detection of the analyte of interest. However, because the literature showed mixed results with the glassy carbon electrode, other electrodes were also investigated, in particular gold, following the work by Saläun [18], and bismuth, investigated by Wang [19]. We kept in mind that in order to develop an in-field voltammetric method for barium, avoiding deoxygenation of the electrolyte/sample solution was an important factor for portability [19].

Pascal Saläun’s [18] successful work with gold electrodes for the detection of antimony and other metal ions provided some merit in trialing the gold electrode for barium; however, our lack of success with barium could be due to the fact that Pascal used acidic electrolytes and/or lack of affinity between the metals. In this work it was not possible to use acidic electrolytes due to the highly negative deposition potential. Wang [19] reviewed bismuth electrodes as an alternative to Hg electrodes. He noted that the two metals (Ba and Bi) have been recently used together in some newer alloys indicating potential affinity between them, which is important for voltammetry.

Voltammetric studies [18, 20] have reported the need to condition the electrode surface when bare electrodes are used in order to activate the electrode for the successful deposition of the required analyte. Conditioning of the electrode means that the electrode is held at a particular potential in a specific electrolyte, usually acidic, for a fixed time or a high concentration of the analyte of interest is run in multiple runs, approximately 10 runs, to ‘activate’ the electrode. Researchers are still studying what happens exactly to the electrode surface during this conditioning step. Current understanding is that the electrode is oxidized and also any contamination such as organics, for example, is being removed during that process [21].

No work has been published on the effect of conditioning of glassy carbon electrode or any other electrode specifically for the deposition of barium. Therefore this study looked at the effect of conditioning on the deposition of barium for bare solid electrodes: gold, glassy carbon, and bismuth. Use of the bare gold electrode was unsuccessful in detecting barium even after multiple conditioning runs using Ba concentrations ranging from 10 𝜇g/L to 1 mg/L and various KCl electrolyte concentrations ranging from 0.01 M to 1.0 M (Figure 1(a)). In contrast, a bare bismuth electrode detected barium after a few conditioning runs but the peak was not sharp and well resolved (Figure 1(b)). Ba peak heights for the bismuth electrode appear comparable to glass carbon electrode but were poorly resolved, large, and rounded (Figure 1(b)). The linear response for barium using in situ Hg on glassy carbon was better than on any other electrode/electrolyte system investigated; however, conditioning of the electrode was required to improve sensitivity (Figures 1(c) and 1(d)).

3.1.2. Electrochemical Parameters Optimization. KCl was chosen as the supporting electrolyte for its neutral pH, low toxicity, and capacity to resist electrolytic breakdown until approximately -2900 mV during scanning. The typical concentration for electrolytes is 0.1 M or higher to ensure good conductance [22, 23], but in this case, we found that 0.02 M KCl allowed for multiple runs without immediate gas evolution obscuring the signal.
Two different types of voltammetric methods were investigated here: linear sweep (LS-ASV) and differential pulse (DP-ASV). Both methods produced a barium signal; however, the baseline resolution and sensitivity of the barium peaks was improved with differential pulse technique (as shown in Figure 2). Consequently, differential pulse potential delivery was chosen for this study.

During potential delivery investigation, scan rate was also tested and although values for peak heights were larger using a 50 mV/s scan (sweep) rate (DP-ASV), better peak resolution and smoother baseline was found at 100 mV/s (DP-ASV). Thus, 100 mV/s was chosen as the optimal scan rate (Figure 2). Interestingly, with LS-ASV, the baseline noise was indistinguishable from the barium peak below 500 mV/s and above 500 mV/s scan rate, and it was found that the response was not linear. A nonlinear response at fast sweep rates has been attributed to slower reaction kinetics in studies with copper, reported by Wu [24]; this is possibly the case here with barium.

Deposition potential (dp) was initially investigated with 0.05 M KCl using differential pulse at 100 mV/s from dp = -3000 mV to dp = -2300 mV with Ba standard 10 μg/L (Figure 3). Deposition times (t_{dep}) were 10, 30, 60, and 120 sec for each potential. A 30 sec, 0.05 M KCl / 5 mg/L Hg blank for each deposition potential (dp) was used. The optimum dp for Ba was clearly -2500 mV, and when each was tested, dp = -2500 mV showed better stability and reproducibility over multiple runs compared to dp = -2400 mV.

From the thorough investigation of the various voltammetric parameters, the optimum parameters were glassy carbon electrode with 5mg/L Hg (GCE + Hg) 0.02 M KCl, deposition potential (dp) -2500 mV, 100 mV/s, deposition time (t_{dep}) of 30 seconds.

3.2. Method Validation. The validation of the barium method was obtained by determining the limit of detection, reproducibility, error intervals, linear working range, uncertainty, and comparison with ICP-MS.

3.2.1. Linear Working Range. To determine linear working range for barium analysis, barium concentrations between 10 μg/L and 160 μg/L were analysed in 0.02 M KCl with Hg 5 mg/L electrolyte, using differential pulse, with dp = -2500 mV, scan rate= 100 mV/s, and a deposition time of 30 sec (Figure 4).

3.2.2. Limit of Detection. The limit of detection (LOD) and limit of quantification (LOQ) were determined using the following formulas [25, 26]:

\[ \text{LOD} = 3s/m \]

\[ \text{LOQ} = 10s/m \]

where 3 corresponds to a confidence level of 98.3%, s is the standard deviation of the blank, and m is the slope of the linear plot of concentration vs. current. Using the three replicates of the blank run, the standard deviation was determined by using the peak current values. The standard deviation of the triplicate blanks is 0.1527 and the slope of the calibration line is 0.2688 (as shown in Figure 4); therefore, LOD = 1.72 μg/L and LOQ = 5.7 μg/L.

The LOD is low enough to allow dilution of samples, which will minimize the susceptibility of the method to matrix effects, by effectively diluting them out.

It was possible to detect 1μg/L of barium using differential pulse, t_{dep} = 120 sec, dp = -2500V, 100mV/s in 0.02 M KCl with 5 mg/L Hg as shown in Figure 5.

3.2.3. Reproducibility and Uncertainty of Measurement. The optimized method utilising GCE with Hg in situ was employed to detect Ba over multiple runs. For 10 measurements performed for Ba concentration of 20 μg/L (Figure 6) the mean peak height was 19.08 ± 1.12 μA and a relative standard deviation of 5.87 % was obtained.
3.3. Method Application

3.3.1. Water Sample Analysis. Various types of Western Australian drinking water samples were collected for analysis by voltammetry with the expectation of finding little or no barium in them. In the event of a null result, control samples were spiked with Ba standard of known quantity and analysed in order to verify the feasibility of the method. The samples were tap water, bore water, bottled water, and a sample from a rainwater tank. Barium content was highly variable between water samples, ranging from 7.59 ± 0.1 µg/L in bottled water to 73.94 ± 1.57 µg/L in Bullsbrook bore water and up to 464.56 ± 28.15 µg/L in Wangara bore water (Table 1). Voltammetric analyses were quite variable between sample replicates, RSD being as low as 1.1% and as high as 49.5% across ten samples. None of the concentrations exceeded the WHO guideline threshold of 700 µg/L [4]. ASV results were in excellent agreement with ICP-MS data with less than 5% difference as shown in Table 1.

The voltammograms of water samples revealed some interference at the barium stripping region in the bore water and tap water samples compared with rainwater and bottled water. Some Ba peaks shifted or peaks became part of a large shoulder making it more difficult to distinguish from the curve of the baseline. The presence of high alkalinity or calcium content in those samples could be the cause or suppressive effects from other metals not accounted for in the ICP-MS analysis and is in agreement with effects reported by Wang [21] during ASV studies on alkaline earth metals.

3.3.2. Brake Pad Analysis. Ba concentration was very high in the brake pad dust samples (Table 2), requiring substantial dilution, reducing matrix interferences to negligible during voltammetric analyses, despite acidification of samples to extract the metals. The ASV results were in excellent agreement with the ICP-MS data with the largest % difference being less than 10% and smallest less than 1% (Table 2).

Table 1: Total Ba concentrations determined in 10 drinking water samples, taken from municipal tap water, bores, a rainwater tank, and bottled water in Western Australia. [a] 1. Bottled water (Mt Franklin brand), 2. Rainwater (tank), 3. Drinking fountain water (ECU campus), 4. Tap water (Wanneroo residence), 5. Filtered tap water (Wanneroo residence), 6. Bore (Wangara), 7. Bore (Bullsbrook) 1, 8. Bore (Bullsbrook) 2, 9. Bore (Craigie), and 10. Bore, (Muchea). The F value calculated for these samples is 0.99034.

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<th>Sample</th>
<th>ASV Mean (µg/L n=3)</th>
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<th>ICP-MS (µg/L)</th>
<th>% Differ. ASV vs. ICP</th>
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Brake pad analysis results support the potential of this ASV method developed to be robust and accurate enough for even these rather complicated matrix samples.

4. Conclusion

Electrode conditioning is clearly an important part of voltammetry for some metals such as barium and antimony and the phenomenon is worth further research. The bismuth electrode showed some promise and also merits future investigation. The optimized method developed here performed best on water and brake pad samples due to minimization of matrix-derived interferences.

A rapid barium detection method could be an advantage for environmental consultants, because it would allow for monitoring of water supplies in the vicinity of oil and gas fracking activities. Trace metal detection of barium can also be used as an indicator of vehicle brake pad deterioration.

Data Availability

All data is available within the paper.

Disclosure

The work presented here is partly from an Honours Thesis by Mrs Samantha Ridgway (https://ro.ecu.edu.au/theses_hons/1472/).

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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