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A sensitive procedure for the rapid determination of arsenic(III) by flow injection analysis and chemiluminescence detection

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Abstract

A novel chemiluminescence flow injection procedure for the determination of As(III) in aqueous samples is described. The method involves injection of As(III) samples into a 1% (m/v) sodium hexametaphosphate in 0.02 M H_2SO_4 carrier stream, which then merges at a Y-piece with a reagent stream consisting of potassium permanganate (5.0×10^{-5} M) made up in the acidic sodium hexametaphosphate carrier solution. The chemiluminescence intensity of the resulting reaction mixture was measured at a photomultiplier tube operated at a voltage of 0.93 kV. Under optimized conditions, the method is characterised by a linear range from 0.5 to 5.0 $\mu g\,l^{-1}$, a detection limit of 0.3 $\mu g\,l^{-1}$ and a sampling frequency of 150 h^{-1}. The effects of common anionic and cationic interferences were investigated, and it was found that the only ions to cause serious interference were those which react with potassium permanganate, namely sulphide, iodide and ferrous.

Keywords: Flow injection; Chemiluminescence; Arsenic; Acidic potassium permanganate

1. Introduction

Arsenic occurs in the environment in many and varied organic and inorganic forms. In ground and surface waters, arsenic is generally found in the inorganic forms of arsenite (As(III)) and arsenate (As(V)), both of which are acutely toxic if swallowed. Ingestion of large doses leads to gastrointestinal, cardiovascular and nervous system disfunction and eventually death. Long-term exposure to low concentrations of arsenic has been linked to increased risks of cancer. With the exception of occupational exposure by inhalation, arsenic is generally introduced to the body through the ingestion of food and water [1]. Concentrations of arsenic in surface and ground waters generally range from 1 to 10 $\mu g\,l^{-1}$, but elevated levels (100–5000 $\mu g\,l^{-1}$) have been reported in groundwaters in China [2], and India and Bangladesh [3]. Consequently the World Health Organisation has identified an urgent requirement for the development of simple, low-cost equipment for field measurement of arsenic [4]. The maximum contaminant level (MCL) of arsenic in drinking water recommended for implementation in 2006 in the USA is 10 $\mu g\,l^{-1}$ [5] and the MCL for Australia is 7 $\mu g\,l^{-1}$ [6].

There are several accepted analytical methods currently available for the measurement of arsenic in environmental samples. These include atomic fluorescence spectrometry (AFS) [7], graphite furnace atomic absorption spectrometry (GFAAS) [8], hydride generation atomic absorption spectrometry (HGAAS) [9], inductively coupled plasma atomic emission spectrometry (ICP-AES) [10] and inductively coupled plasma mass spectrometry (ICP-MS) [11]. However, these methods require comparatively expensive equipment and they are not readily amenable to portable instrumentation.

Flow injection (FI) analysis has proved to be suitable for on-line analysis because of its low reagent and sample consumption, high sampling frequency and ease of automation [12,13]. Spectrophotometric determination based on the formation of molybdenum blue has been used by several workers for the detection of arsenate in FI [14–16]. Linares et al. described

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a method for the determination of arsenate in the presence of arsenite and phosphate [14], Narusawa detected arsenate in the presence of silicate and phosphate after anion exchange separation [15] and Frenzel et al. determined arsenate in mixtures containing silicate, arsenate, arsenite and phosphate after chromatographic separation [16].

Pervaporation-flow injection (PFI) is now an established technique for the determination of volatile or semi-volatiles in ‘dirty’ environmental samples [17–20]. Hydride generation was combined with PFI for the sensitive determination of As(III) in aqueous environmental samples, using molybdenum blue detection in one report [17] and permanganate detection in the other [18]. PFI has also been combined with hydride generation and AFS detection for speciation of As(III) and As(V) in dirty samples [19] and extractable arsenic in soils [20].

Numerous reports have appeared on the use of chemiluminescence detection in FI for the determination of organic and inorganic species, and the majority of these investigations have been based on the oxidation of luminol by hydrogen peroxide [21]. We are aware of only two reports on the determination of inorganic arsenic species using luminol-based chemiluminescence in FI [22,23]; one claims a detection limit of 8 μg l^{-1} [22] and the other a detection limit for both As(III) and As(V) of 100 μg l^{-1} [23].

Hindson and Barnett reviewed the use of acidic potassium permanganate as a promising chemiluminescence reagent for the determination of inorganic species [24]. In the present paper, we wish to report the first use of this reagent for the sensitive determination of arsenite and likely interferences are investigated.

2. Experimental

2.1. Reagents and solutions

All reagents were of analytical reagent (AR) grade and were used as received. Tris(2,2′-bipyridyl)ruthenium(II) dichloride hexahydrate was synthesised in our laboratories from ruthenium trichloride (Johnson Matthey Chemicals, UK) by reaction with 2,2′-bipyridine (Sigma–Aldrich, USA) as reported previously by Broomhead and Young [25].

Potassium permanganate stock solution (1.0×10^{-2} M) was prepared by dissolving 0.1587 g of $KMnO_4$ (BDH, UK) in 100 ml deionised water. The carrier stream solution containing 1% (m/v) of sodium hexametaphosphate was prepared daily by dissolving the appropriate amount of sodium hexametaphosphate (Sigma–Aldrich, USA) in 0.02 M sulphuric acid solution. The reagent stream solution, acidic potassium permanganate (5.0×10^{-5} M), was prepared fresh daily by making appropriate dilution of the $KMnO_4$ stock solution in carrier solution. Both solutions were filtered through 0.45 μm nylon filters (Alltech, Australia) and sonicated for 10 min before use. NANOpure deionised water (17.9 MΩ cm, Barnstead, USA) was used for all solution preparations.

Arsenic(III) stock solution (1000 mg l^{-1}) was prepared by dissolving 0.1734 g of $NaAsO_2$ (Ajax, Australia) in 100 ml of deionised water. Standard solutions of As(III) (0.5 μg l^{-1}–25.0 mg l^{-1}) were made up daily by making appropriate dilutions of the As(III) stock solution (1000 mg l^{-1}) with the carrier solution. The stock solution of As(III) was kept in a sealed container in a refrigerator at 4 °C when not in use.

2.2. Chemiluminescence instrumentation

The FI manifold used in all experiments is illustrated in Fig. 1. The experimental setup consisted of a four-channel peristaltic pump with rate selector (Minipuls 3, Gilson, France), a sample injection valve (Type 50, Rheodyne Inc., California, USA) and PTFE connection tubing (0.5 mm i.d.). The chemiluminescence signal was monitored in a custom built flow-through luminometer, which consisted of a flat spiral glass flow cell (glass tubing i.d. 1.5 mm, spiral coil diameter 25 mm) mounted flush against a red sensitive photomultiplier tube (PMT) (Thorn-EMI 9878SB, Electron Tubes Ltd., UK). The operational potential for the PMT was provided by a stable power supply (Thorn-EMI model PM20D, Electron Tubes Ltd., UK). The flow cell, photomultiplier tube and voltage divider were encased in light tight housing. The detector output was recorded on a strip chart recorder (Kipp & Zonen, The Netherlands) and the chemiluminescence response was measured manually using peak height of the transient response. pH measurements were obtained using an Orion 720 IonAnalyzer (Orion, USA) with a combined glass electrode.

2.3. Procedure

The peristaltic pump was employed to propel the reagent and carrier streams at equal flow rates with a total flow rate of

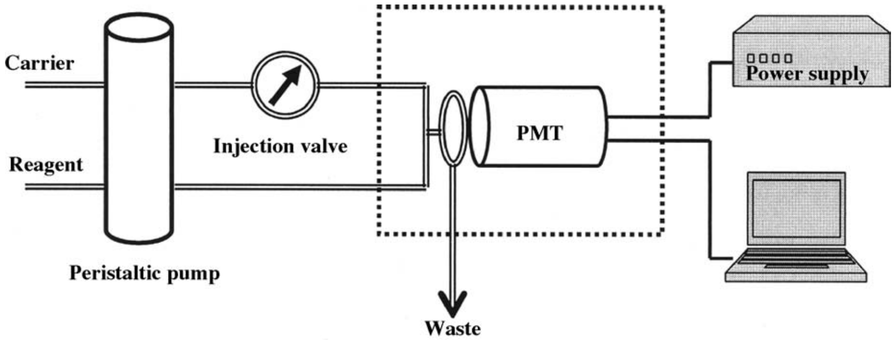

Fig. 1. Schematic diagram of the chemiluminescence FI manifold.