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Gas-diffusion flow injection determination of Hg(II) with chemiluminescence detection

Nazanin Amini, Spas D. Kolev*

School of Chemistry, The University of Melbourne, Victoria 3010, Australia

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Abstract

A gas-diffusion flow injection method for the chemiluminescence detection of Hg(II) based on the luminol–H_2O_2 reaction was developed. The analytical procedure involved the injection of Hg(II) samples and standards into a 1.50 M H_2SO_4 carrier stream, which was subsequently merged with a reagent stream of 0.60% (w/v) $SnCl_2$ in 1.50 M H_2SO_4 to reduce Hg(II) to metallic Hg. The gas-diffusion cell was thermostated at 85 °C to enhance the vaporisation of metallic Hg. Mercury vapour, transported across the Teflon membrane of the gas-diffusion cell into the acceptor stream containing 1.00×10^{-4} M $KMnO_4$ in 0.30 M H_2SO_4, was oxidised back to Hg(II). The acceptor stream was merged with a reagent stream containing 2.50 M H_2O_2 in deionised water and then the combined stream was merged with another reagent stream containing 7.50×10^{-3} M luminol in 3.00 M NaOH at a confluence point opposite to the photomultiplier tube of the detection system. The chemiluminescence intensity of the luminol–H_2O_2 reaction was enhanced by the presence of Hg(II) in the acceptor stream. The corresponding increase was related to the original concentration of Hg(II) in the samples and standards. Under optimal conditions, the chemiluminescence gas-diffusion flow injection method was characterised by a linear calibration range between 1 $\mu g\,L^{-1}$ and 100 $\mu g\,L^{-1}$, a detection limit of 0.8 $\mu g\,L^{-1}$ and a sampling rate of 12 samples per hour. It was successfully applied to the determination of mercury in seawater and river samples.

Keywords: Gas-diffusion flow injection analysis; Mercury determination; Cold vapour; Chemiluminescence detection; Luminol–permanganate reaction; Luminol–hydrogen peroxide reaction

1. Introduction

Numerous highly sensitive and selective analytical techniques for detection of mercury in water samples (e.g., neutron activation analysis [1], atomic fluorescence spectrometry [2], cold vapour atomic absorption spectrometry, CV-AAS [3], inductively coupled plasma optical emission or mass spectrometry [4]) are currently used in analytical practice. The majority of these techniques employ large and expensive instrumentation and do not allow the construction of portable analysers for on-site mercury monitoring.

Flow injection (FI) analysers with online gas-diffusion (GD) [5] or pervaporation [6] separation are suitable for the selective determination of volatile or semi-volatile analytes or analytes which can be converted chemically to volatile chemical species. Despite the fact that mercury vapour is the key feature of CV-AAS, one of the most frequently used analytical techniques for the determination of Hg(II), there are only a few GD–FI methods [7–10] for the determination of Hg(II) involving mercury vapour generation. Two of these methods [7,8] are not suitable for the construction of portable analysers because of the use of atomic absorption [7] or atomic fluorescence [8] detection. The other two GD–FI methods, developed recently in our laboratory, utilize smaller and inexpensive detectors (i.e., spectrophotometric [9] and amperometric [10]) and the corresponding GD–FI systems are amenable to miniaturization. The detection limit of the spectrophotometric method is 4 $\mu g\,L^{-1}$ [9] while that of the amperometric method is 0.9 $\mu g\,L^{-1}$ [10] thus making it suitable for drinking water monitoring (e.g., maximum allowed concentration of mercury in drinking water is 2 $\mu g\,L^{-1}$ and 1 $\mu g\,L^{-1}$ according to the US National Primary Drinking Water Standards [11] and the Australian Drinking Water Guidelines [12], respectively). The amperometric detector, however, required prolonged periods of conditioning before a stable baseline had been established. This is a common disadvantage of electrochemical methods compared

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* Corresponding author. Tel.: +61 3 8344 7931; fax: +61 3 9347 5180.
E-mail address: s.kolev@unimelb.edu.au (S.D. Kolev).

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to optical methods. A relatively inexpensive optical method, which generally offers high selectivity and sensitivity is chemiluminescence detection. Numerous studies have been reported on the use of chemiluminescence detection in FI systems for the determination of various analytes, with the chemiluminescence reaction between luminol and H_2O_2 in alkaline medium being used in most cases [13]. A number of transition metal ions (e.g., Co(II), Cu(I), Fe(II) and Fe(III)) [14,15], including Hg(II) [16], catalyze this reaction and this has been used for the development of sensitive chemiluminescence methods for their detection. FI methods for the determination of mercury based on other chemiluminescence reactions have also been reported [17,18]. One of them is based on the catalytic effect of the Hg(II)–EDTA complex on the reaction between luminol and dissolved oxygen [17] while in the other one Hg(II) accelerates the decomposition $K_4Fe(CN)_6$ [18]. The detection limits reported for these two methods were $30\,\mu g\,L^{-1}$ and $0.22\,\mu g\,L^{-1}$, respectively.

This paper reports on the development and optimisation of a sensitive and selective GD–FI method with chemiluminescence detection based on the catalytic effect of Hg(II) on the luminol–H_2O_2 reaction. The experimental GD–FI system was applied for the determination of Hg(II) in environmental aqueous samples.

2. Experimental

2.1. Solution preparation

All chemicals were of analytical grade and were used as received. Deionised water (Millipore Synergy, France) was used for all solution preparation. Solutions of sulfuric acid, sodium and potassium hydroxide were prepared by appropriate dilutions of concentrated sulfuric acid (BDH, Australia) or dissolution of solid sodium (Univar, Australia) or potassium (Univar, Australia) hydroxide. Mercury(II) stock solution ($1000\,mg\,L^{-1}$) was prepared by dissolving 0.147 g $HgSO_4$ (Univar, Australia) in 100 mL 1.5 M H_2SO_4. Mercury(II) standards in the concentration range from $0.100\,\mu g\,L^{-1}$ to $1.00\,mg\,L^{-1}$ were prepared daily by making appropriate dilutions of the stock solution with 1.50 M H_2SO_4 solution. Potassium permanganate stock solution ($1.00 \times 10^{-2}\,mol\,L^{-1}$) was prepared by dissolving 0.158 g $KMnO_4$ (Chem-supply, Australia) in 100 mL 0.30 M H_2SO_4. Potassium permanganate working solutions (1.00×10^{-6}–$5 \times 10^{-4}\,mol\,L^{-1}$) were prepared by diluting the potassium permanganate stock solution with 0.10–0.45 M H_2SO_4 solutions. Hydrogen peroxide working solutions (0.50–3.50 $mol\,L^{-1}$) were prepared by appropriate dilutions of 30% hydrogen peroxide (Univar, Australia) with deionised water. These working solutions were stored in sealed reagent bottles, wrapped in aluminium foil for light protection. Luminol working solutions (1.00×10^{-5}–$4.00 \times 10^{-3}\,mol\,L^{-1}$) were prepared by dissolving luminol (Fluka, Switzerland) in 0.50–4.00 NaOH (Univar, Australia) solutions and stored in amber glass reagent bottles. Tin(II) chloride working solution was prepared by dissolving 0.600 g $SnCl_2$ (Sigma, Germany) in 1.50 M H_2SO_4. All working solutions were prepared daily.

Stock solutions containing $1.00 \times 10^3\,mg\,L^{-1}$ Cu(II), Se(IV), As(III), Ag(I) or CH_3Hg^+ were prepared by dissolving 0.392 g $CuSO_4{\cdot}5H_2O$ (BDH, Australia), 0.279 g $SeCl_4$ (Aldrich, USA), 0.173 g Na_3AsO_3 (Sigma, Germany), 143 g Ag_2SO_4 (BDH, England), or 0.100 g CH_3HgCl (Aldrich, USA) in 100 mL 1.50 M H_2SO_4. Standard solutions of these compounds were prepared by appropriate dilutions of the corresponding stock solutions with 1.50 M H_2SO_4 solution and used in the interference studies.

Reagent solutions used in the determination of mercury by CV-AAS were 0.40% (w/v) $NaBH_4$ (Labchem, Australia) in 0.50% (w/v) NaOH (Univar, Australia) and 5.00 M HCl (BDH, England).

The two components of the Fenton's reagent (i.e., Fe(II) and H_2O_2) used in the digestion of organic mercury in water samples were a saturated solution of ammonium iron(II) sulfate (Univar, Australia) and a 30% H_2O_2 (Univar, Australia) solution [19].

2.2. Samples

Sea water and fresh water samples were collected from Port Kembla bay (New South Wales, Australia) and Yarra River (Victoria, Australia), respectively. All samples contained fine suspended particulate matter and coloured compounds and were analysed for mercury before and after digestion. Direct injection of these samples into the GD–FI system did not result in blockages. However, these samples were filtered prior to the CV-AAS analysis as required by the instrument manufacturer. Since no mercury was detected in the original river samples, they were spiked with known amounts of Hg(II).

2.3. Experimental procedure

2.3.1. Digestion of aqueous samples

The seawater samples from Port Kembla bay were adjusted to pH between 3 and 4 using 0.05 M H_2SO_4 and 20% (w/v) KOH solutions. Fifty microlitres of saturated ammonium iron(II) sulfate solution and 100 μL 30% H_2O_2 solution were added to 50 mL of each seawater sample. The sample solutions were thermostated at 50 °C in a water bath for 30 min [19].

2.3.2. GD–FI manifold

The GD–FI manifold (Fig. 1) incorporated a rotatory injection valve (Model 5020, Rheodyne, USA) with a 500 μL sample loop, Teflon tubing (0.5 mm i.d., Supelco, USA), a home made GD cell [10] and a chemiluminescence detection system. Mixing coils of 1 m length were used to facilitate mixing between the flow system's streams. Three peristaltic pumps (VS4-10R-Midi, Watson Marlo Alitea, Sweden) furnished with Tygon tubing (TACS, Australia) were initially used (Fig. 1A). The tin(II) chloride reagent stream (R_1) and carrier stream (R_2), which formed the donor stream (R_{donor}) of the GD–FI manifold, were propelled by one of the pumps. A second pump propelled both the potassium permanganate acceptor stream (R_3) and the hydrogen peroxide reagent stream (R_4) while a third one propelled the luminol reagent stream (R_5). Streams R_3–R_5 formed the detection stream (R_{det}) of the GD–FI manifold where the analytical