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On-line preconcentration and recovery of palladium from waters using polyaniline (PANI) loaded in mini-column and determination by ICP-MS; elimination of spectral interferences

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ABSTRACT

The applicability of polyaniline (PANI) for the on-line preconcentration and recovery of palladium from various water samples has been investigated. Batch experiments were performed to optimize conditions such as pH and contact time to achieve quantitative separation of Pd spiked at high ($\mu g\,ml^{-1}$) and low levels ($ng\,ml^{-1}$). During all the steps of the removal process, it was found that Pd was selectively removed by PANI even in the presence of various ions. Quantitative removal of Pd occured in the entire studied pH range (1–12) and the K_d value was found to be $>10^6$. Kinetic studies show that a contact time of <4 min was adequate to reach equilibrium. The retained Pd was subsequently eluted with a mixture of HCl and thiourea, optimized using a factorial experimental design approach. ICP-OES was used for the micro-level determinations of Pd whereas ICP-MS was used for the determination of Pd at sub-ppb levels.

Breakthrough curve using column experiments demonstrated that PANI has an excellent ability to accumulate up to ~120 $mg\,g^{-1}$ of Pd from synthetic sample solutions. A preconcentration factor of about 125 was achieved for Pd when 250 ml of water was passed. PANI columns prepared were used up to 10 times in consecutive retention–elution cycles without appreciable deterioration in their performance. The proposed on-line method also has the ability to remove interfering elements Cu and Y for the determination of Pd in waters by ICP-MS. The reported method has been applied successfully for the determination of Pd in ground water, lake water sea-water and waste water samples. The recoveries were found to be >95% in all cases. These studies indicate that PANI has an excellent ability to preconcentrate Pd from various waters making the method very promising for the determination of Pd.

1. Introduction

In recent years, palladium has found a variety of applications (e.g. medicine and dentistry (25–40% of annual consumption); electrical products and electronics (30–40%), chemical industry (10–15%), automotive industry (5–15%), jewelry (2–5%), glass industry, etc.) because of its attractive physical and chemical properties such as high melting point, corrosion resistance and extraordinary catalytic properties [1–4]. Although the benefits of automotive catalysts are undisputable, they result in significant amounts of Pt, Rh and Pd being released into the atmosphere leading to contamination of food and water-bodies [5,6] which finally lead to bioaccumulation in the living organisms through diverse pathways. Although Pd in its elemental form is rather inert with respect to its biological activity, all ionic species of Pd are regarded as highly toxic and carcinogenic to humans, causing asthma, allergy, rhinoconjunctivitis, etc. [7,8]. But, the trends in their production, demand and prices show that there has been a significant growth in the demand for PGMs, particularly palladium, over the years [9]. In order to meet this increasing demand and in view of the limited resources, there is a need to look for new sources of palladium. One way is to recover and recycle Pd from various wastewaters generated from industries that use PGEs extensively. This process also contributes significantly to the protection of the environment by reducing any negative impact associated with metal waste disposal. Therefore, the development of new methods for the effective separation, preconcentration and determination of Pd in waters has been of a great interest.

Palladium in environmental matrices, in particular waters, usually occurs at sub-ppb levels [10] and its direct measurement is often difficult even with highly sensitive and selective techniques such as inductively coupled plasma-mass spectrometry (ICP-MS), electro-thermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma optical emission spectrometry (ICP-OES) [11–13] due to matrix and spectral interferences. Therefore, coupling of a separation/preconcentration procedure and

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elimination of interfering species in single step prior to detection is necessary.

Fire assay, solvent extraction, co-precipitation, ion-exchange and solid-phase extraction (SPE) techniques have been employed widely for the preconcentration of Pd [14–16]. Among the techniques reported, column configuration SPE has found increasing application for the preconcentration of trace amounts of Pd and effective elimination of matrix interferences prior to analysis because of high selectivity, high enrichment capacity and operational simplicity [12,13]. Different sorbents such as Amberlite XAD resins [17,18], alumina [19], modified silica gel [20,21] and various chelating resins such as Metalfix-Chelamine [13,22], dithiozone anchored poly(vinylpyridine) [23] have been extensively used for the preconcentration of palladium from aqueous media. In recent years, a variety of anion-exchange resins for the removal and preconcentration of palladium have also been reported in the literature [24,25].

Along with complex-forming and ion-exchange sorbents, a number of different sorbents such as natural and synthetic zeolites, activated carbon [26] and biosorbents, etc. [27,28], have been employed. But most of the reported methods suffer from various disadvantages such as high cost of the sorbents, high detection limits, low enrichment factors, poor reusability of the sorbents, need for large amount of organic reagents and generation of large volumes of secondary wastes. Thus there is a need for developing a method that can overcome these limitations.

Polyaniline (PANI) is well known for its ion-exchange and conducting properties [29,30]. Applicability of PANI as ion-exchange resin and conducting polymer, has attracted a considerable scientific interest in recent decades because of its good combination of properties, diverse structure, thermal and radiation stability, low cost, ease of synthesis and thus resulted in its wide applications in different fields such as micro-electronics, corrosion protection, sensors and electrodes for batteries [29,31–33]. PANI can be easily synthesized either chemically or electrochemically from acidic solutions [29,31]. PANI can exist in various oxidation states characterized by the ratio of imine to amine nitrogen. Upon alkaline treatment of the polymer with dilute NH_3 or NaOH solutions, it changes into a material called emeraldine which comprises an equal number of repeating reduced and oxidized units.

The physicochemical properties of polyaniline and its potential applications in diverse fields have been reviewed [29,31]. PANI has been used as base material for the preparation of mercury standard for use in neutron activation analysis [34]. The applicapability of polyaniline for the separation and determination of Cd, Cu, Pb and Sb in KI medium in biological matrices was also studied [35]. In our earlier studies, PANI was applied successfully for the removal and speciation of inorganic and methylmercury in waters [36]. More recently, studies were conducted to evaluate the performance of PANI synthesized on jute surface for the removal of hexavalent chromium [Cr(VI)] in aqueous environment [37]. Despite the extensive literature on various applications of PANI, to our knowledge, no application of PANI for preconcentration and removal of Pd from waters has been reported.

This paper deals with the potential application of polyaniline as an anion exchanger suitable for environmental protection through water and wastewater treatment. In this work, the efficacy of PANI, probably for the first time, has been investigated for the removal and preconcentration of low levels of palladium from various waters such as ground waters, lake waters, sea-waters and wastewaters. After optimizing all the experimental parameters such as influent pH, equilibration time, eluent composition, etc., using batch experiments, extensive studies were carried out with PANI loaded in home made mini-column for preconcentration of Pd and elimination of interfering species followed by optimization of the eluent volume. Using this optimal procedure, capacity studies were carried out using a breakthrough curve.

Table 1a
Instrumental and operating parameters of ICP-MS.

Instrumental parameters	Scanning parameters
Coolant gas: 13.4 l min^{-1}	Scanning mode: peak jump
Aux. gas: 0.88 l min^{-1}	Number of replicates: 3
Nebulizer gas: 1.06 l min^{-1}	Dwell time: microsec/channel 300
Sampler cone: 1.0 mm Ni	Sample delay: 30 s
Skimmer cone: 0.7 mm Ni	Stabilization delay: 20 s
Torch type: Fassel	Rinse time: 30 s
Plasma FW power: 1350 W	Sample pump rate: ~1.0 ml min^{-1}
Reflected power: <5 W	Isotopes used: m/z 105, 106, 108

2. Experimental

2.1. Instrumentation

Palladium concentrations when at sub-ppb levels were determined using an ICP-MS (VG Plasma Quad 3, VG Elemental, Winsford, Cheshire, U.K.) system. The data were collected by monitoring the most abundant isotopes of Pd m/z 105, 106 and 108 using the peak jump mode. For the experiments with on-line preconcentration, a time resolved mode of data acquisition available with the Plasma Quad was used for obtaining a chromatogram. The optimized conditions are given in Table 1a. The experimental set-up for on-line preconcentration and spectral interference studies of Pd is shown in Fig. 1a and b respectively.

A 1 kW power, Model JY-2000 ICP optical emission spectrometer (Jobin Yvon, France) was used for the determination of Pd using the 340.548 nm emission line. The ICP-OES system was equipped with a Meinhard concentric nebuliser and a cyclonic spray chamber. The instrumentation and operating conditions are given in Table 1b.

2.2. Reagents and standards

All chemicals were of analytical grade unless stated otherwise. Sub-boiled HCl and HNO_3 were prepared in our laboratory by sub-boiling distillation in quartz stills and used wherever necessary. Ultrapure water (>18 MΩ-cm resistivity), obtained using a Milli-Q system (Millipore Corporation, USA), located in class 100 area, was used for preparation of standards, for preparing samples and for final rinsing of the acid cleaned vessels. All containers were soaked in 20% HNO_3 and cleaned thoroughly with high purity water prior to use. Thiourea (Merck, Darmstadt, Germany), a non-polluting reagent which has been widely used for extracting precious metals [38,39] and preparation of thiourea-based coordinating resins for binding of palladium as well as an eluent [13,22], was used along with HCl in the present elution studies. Working standards were prepared just before use by appropriate dilution of the stock standard solutions.

All the pH adjustments were done with very dilute solutions of HCl and NaOH. The mean values of the measurements for duplicate samples were used for calculations and the mean values are within

Table 1b
Instrumentation and operating conditions of ICP-OES.

Parameters	Operating conditions
Plasma gas flow rate	13 l min^{-1}
Carrier gas	1.2 l min^{-1}
Sample uptake rate	1.0 ml min^{-1}
R.F. generator	900 W, frequency 40.6 MHz
Monochromator	0.64 M, 2400 line mm^{-1}, Czerny turner mounting
Torch	Jobin Yvon demountable quartz with argon sheathing gas
R.F. forward power	1.05 kW (<10 W reflected power)