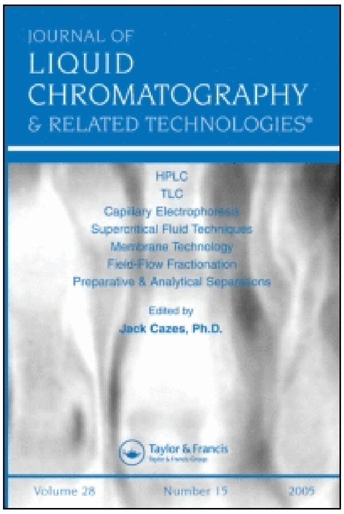

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Method for the Determination of Cu(II), Ni(II), Co(II), Fe(II), and Pd(II) at ppb/subppb Levels by Ion Chromatography

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To cite this Article Bruno, Paolo , Caselli, Maurizio , Daresta, Barbara Elisabetta , de Gennaro, Gianluigi , de Pinto, Valentina , Ielpo, Pierina and Placentino, Claudia Marcella(2007) 'Method for the Determination of Cu(II), Ni(II), Co(II), Fe(II), and Pd(II) at ppb/subppb Levels by Ion Chromatography', Journal of Liquid Chromatography & Related Technologies, 30: 4, 477 — 487

To link to this Article: DOI: 10.1080/10826070601093762

URL: http://dx.doi.org/10.1080/10826070601093762

Journal of Liquid Chromatography & Related Technologies®, 30: 477–487, 2007

ISSN 1082-6076 print/1520-572X online
DOI: 10.1080/10826070601093762

Method for the Determination of Cu(II), Ni(II), Co(II), Fe(II), and Pd(II) at ppb/subppb Levels by Ion Chromatography

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Abstract: A method for the determination of Cu(II), Ni(II), Zn(II), Co(II), Fe(II), and Pd(II) at ppb/subppb levels by ion chromatography was developed, improving a previous work of the same authors. In order to lower the detection limits, the direct injection of a large sample volume (5 mL) and 4-(2-pyridylazo) resorcinol solution at pH 6, with hexadecylpyridinium chloride as the post-column reagent were used. The obtained calibration curves were linear (for each metal $R^2 \geq 0.99$) with good reproducibility; the detection limits for Cu(II), Ni(II), Zn(II), Co(II), Fe(II), and Pd(II) were 1.1, 0.46, 39, 0.18, 4.5, and 1.7 ppb, respectively.

Keywords: Ion chromatography, Heavy metals, Palladium

INTRODUCTION

The wide use of heavy metals in several productive activities causes the introduction of these elements into the environment. They accumulate in the different environmental compartments and then enter the food chain, damaging natural ecosystems and human health.[1–3]

Among heavy metals released from various products and processes, iron, nickel, cobalt, copper, and zinc are of the greatest concern. They are naturally occurring metals that are found in the environment in low concentrations;

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they are also essential elements for humans and animals in small quantities. However, toxic and carcinogenic effects can result from exposure to higher concentrations for a wide range of life forms.[4] Over the last years, there is increasing interest in the platinum group elements (PGEs), in particular platinum, palladium, and rhodium. These metals are mainly used in a catalyst to remove pollutants from automotive exhaust gases; PGEs are emitted mostly in particle form, due to the thermal cracking and to the mechanical abrasion during the catalytic conversion. There is great interest in the PGEs determination because they may be toxic for living organisms, considering that the concentration levels of these metals are increasing in urban areas.[5–10] Among PGEs, palladium can be considered a marker of vehicular traffic, because it is mostly used in catalytic converters, more than the other PGEs. Moreover palladium is used in dentistry applications, in electronics, and in jewellery. The largest fraction of palladium is recovered as a by-product of copper and nickel sulphide ore refining (Russia and Canada), or as alloys of the PGEs from primary PGE deposits (South Africa and USA).

In order to study and monitor the impact of the different anthropogenic sources of heavy metals on the environment and human health, it is necessary to develop sensitive and reliable analytical methods to obtain their detection in different matrices. The most used analytical techniques for the determination of heavy metals in environmental samples are atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectroscopy, and mass spectrometry (ICP-OES and ICP-MS).[11–13] An alternative method is the ion chromatography (IC), a very common and suitable technique for routine analysis: it allows separation, detection and quantification of several metals in short time. Ion chromatography is preferred in the process check too because of low instrumental and maintenance costs. Moreover, IC sensitivity and reproducibility can be competitive with spectroscopic techniques.[14–16] Most chromatographic methods for palladium determination are based on reversed phase or chelation separation mechanisms,[17–20] but only a few studies employed ionic exchange.

In geological samples chromatographic PGE separation was carried out on cationic exchange resins coupled with ICP-MS.[21,22] Bruzzoniti et al.[23] developed a new method for on-line preconcentration and separation of palladium using anion chromatography (IonPac AS4 column), with a mixture of HCl and $HClO_4$ as eluent, and spectrophotometric detection of complex PdI_4^{2-} at 407 nm. They also performed platinum and palladium separations as anionic chloro complexes, by IonPac AG11 column, using oxalic acid (18 mM) and nitric acid (0.14 M) as eluents, and a quadruple inductively coupled plasma mass spectrometry (q-ICP-MS) for detection.[24] A method for IC determination of eight heavy metals by a bifunctional ionic exchange column (IonPac CS5A) and spectrophotometric detection after post-column derivatization with 4-(2-pyridylazo)resorcinol (PAR), was already developed.[25] Further improvements[26,27] were performed using enrichment procedures[28,29] in order to improve the method sensitivity using large volume loops up to 5 mL. In these conditions it was possible to obtain detection limits of one order of magnitude lower, without losing efficiency and peak resolution. The contribution of Sutthivaiyakit et al.[30] is very important for ppb level determination of Pd. They used a chelating stationary phase to retain palladium, and PAR at pH 6 in the presence of hexadecylpyridinium chloride to detect it at 550 nm. The aim of this paper is to improve the Bruno et al.[25] method with palladium detection, following Sutthivaiyakit et al. suggestions, and working with a large volume loop. The optimized method was tested for linearity, detection limits, and reproducibility for Cu(II), Ni(II), Zn(II), Co(II), Fe(II), and Pd(II) at ppb/subppb levels.

EXPERIMENTAL

Instrumentation

The ion chromatograph used was a model DX 600 (Dionex, Sunnyvale, CA, USA), equipped with a spectrophotometric variable wavelength. A Rheodyne 6-port injection valve was used with different volume loops ranging between 0.2 and 5 mL. The analytical column was IonPac CS5A (Dionex, Sunnyvale, CA, USA) 250 × 4 mm I.D, preceded by a guard column IonPac CG5A (Dionex, Sunnyvale, CA, USA) 50 × 4 mm I.D. The column outlet and the post-column reagent (PCR) were conveyed, through a 3-way connector, to a 375 μL mixing coil followed by the detector cell.

Reagents and Solutions

All reagents were analytical grade. Oxalic acid dihydrate (Fluka, Milwaukee, WI, USA), sodium nitrate (Fluka, Milwaukee, WI, USA), 4-(2-pyridylazo) resorcinol (PAR; Riedel de Haën, Milwaukee, WI, USA), sodium acetate (Carlo Erba, Milan, Italy), acetic acid (Sigma-Aldrich, St. Louis, MO, USA), hexadecylpyridinium chloride (Fluka, Milwaukee, WI, USA), 1-butyl-pyridinium chloride (Acros Organics, Geel, Belgium), ethanol (J.T. Baker, Phillipsburg, NJ, USA). Working solutions were obtained by dilution of single element standard solutions (Cu(II), Ni(II), Zn(II), Co(II), and Pd^{2+}, 1000 mg/L, Fluka, Milwaukee, WI, USA), with deionized water (resistivity >18.2 MΩ cm) produced by a system Milli-Q (Millipore, Bedford, MA, USA). Fe(II) stock solutions (500 mg/L) were freshly prepared by dissolution of $FeSO_4 \cdot 7H_2O$ (p.a. $\geq 99.0\%$, Fluka, Milwaukee, WI, USA).

RESULTS AND DISCUSSION

In Bruno et al.[25] transition metals were separated as cationic and anionic complexes with the oxalate chelating agent, and they were detected as

PAR-metal complexes. In this work, experimental parameters were optimized to determine palladium and other heavy metals in an unique run.

Optimization of Detection Step

Palladium detection needs the use of a post-column reagent (PAR solution) at a suitable pH value. It was verified that the suitable pH value to achieve the formation of Pd-PAR complex is 6, since at higher values there is the formation of palladium hydroxy complexes, while at lower pH values the concentration of PAR complexing forms decreases. For this reason, an acetate buffer solution 0.1 M at pH 6 was used to prepare PCR. Then, spectrophotometric detection wavelength was investigated. Free PAR has a maximum of absorption at 411 nm, while Pd-PAR complex (pH 6) at 515 nm. In an equimolar solution of Pd(II) and PAR (i.e., 0.01 mM), the Pd-PAR complex absorption (at 515 nm) slowly increases until it reaches a stable value after 50 minutes. Because of the slow kinetic of complexation, the time from eluate and PCR mixing to the detection is not enough to obtain appreciable complex formation. An increase of reaction coil volume favours complexation, and allows obtaining a higher sensitivity, with the disadvantage to increase considerably analysis times. So the post-column reagent composition was changed adding hexadecylpyridinium chloride.[30]

This surfactant in the PCR solution increased the absorbance of 20 times in comparison with the PAR solution at pH 6. The use of hexadecylpyridinium chloride could reduce the time needed to reach equilibrium. In this way, the Pd-PAR signal is increased because in reaction coil bigger complex amount is formed, as observed for platinum(II).[31] Replacing hexadecylpyridinium chloride with 1-butyl-pyridinium chloride, in the same concentration and analytical conditions, it was observed that results are the same compared to the absence of surfactant. It can be supposed that the long hydrophobic alkylic chain of the surfactant molecule has a positive effect on the Pd-PAR complex formation or on its light absorption mechanism. It was verified that an increasing of surfactant concentration does not imply an absorbance enhancement.

Sutthivaiyakit et al. carried out the Pd-PAR complex detection at 550 nm,[30] while Bruno et al.[25] worked at 530 nm, a detection wavelength of 540 nm was selected because it is an optimal trade-off to determine palladium and other heavy metals. Keeping the analytical conditions of Bruno et al. and carrying out the detection at 540 nm with a PCR containing hexadecylpyridinium, palladium was detected at a retention time of 7 minutes.

Sample and Injection Volume

The sensitivity of the method was increased using a sample loop of 5 mL.[26] This enhancement allowed an increasing of chromatographic signal of about

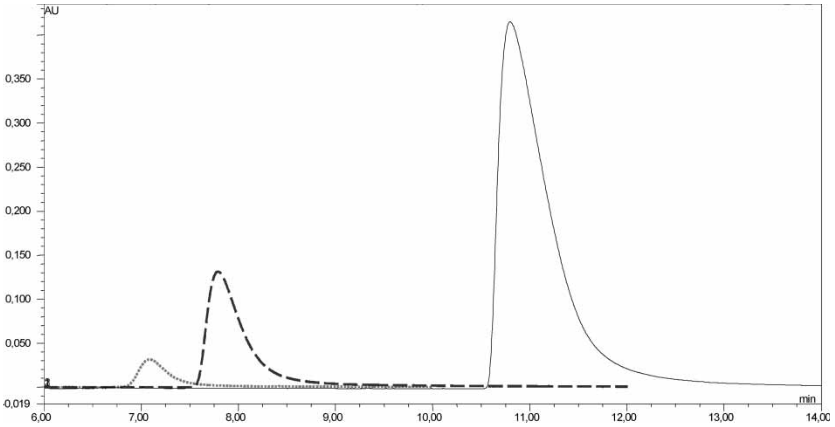

Figure 1. Comparison of three chromatograms of a Pd(II) standard solution (1 ppm) obtained by different loop volumes. Loop volumes: 200 μL (dotted line), 1000 μL (broken line), 5000 μL (continuous line).

twenty-five times. Figure 1 shows that using loop volumes of 0.2, 1, and 5 mL, the palladium elution time changes from 7 to 7.8 and 11 minutes, respectively, without significant chromatographic peaks broadening. We verified whether sample pH affects mobile phase pH in the column, i.e., the ionic exchanges and separation, because the volume of the column and sample are of the same order of magnitude. In order to assess this effect, palladium standard solutions in deionized water and in 0.01 M HCl were prepared and then analyzed. Chromatographic analysis did not show significant differences in signal intensity and retention time between the two solutions. Therefore, the optimized chromatographic conditions were:

Loop volume: 5 mL; Eluent: oxalic acid (28 mM) and sodium nitrate (250 mM); Guard column: IonPac CG5A; Analytical column: IonPac CS5A; Reaction coil: 375 μL; Eluent flow: 1.2 mL/min; PCR: PAR, 0.39 mM, in acetate buffer at pH 6 and of hexadecylpyridinium chloride, 6.6 mM (a stock hexadecylpyridinium chloride solution was prepared by dissolving the salt in ethanol, 10% w/w solution); PCR flow: 0.6 mL/min; Detection wavelength: $\lambda = 540$ nm.

Analytical Performance of the Method

Using optimized analysis conditions to determine palladium, it was possible to detect Cu(II), Ni(II), Zn(II), Co(II), and Fe(II) too, as shown in the chromatogram in Figure 2. In order to evaluate the method's analytical features, linearity, detection limits, and reproducibility for Cu(II), Ni(II), Zn(II), Co(II), Fe(II), and Pd(II) were tested, close to detection limits. In Table 1, for each investigated metal, parameters of regression lines are shown. The

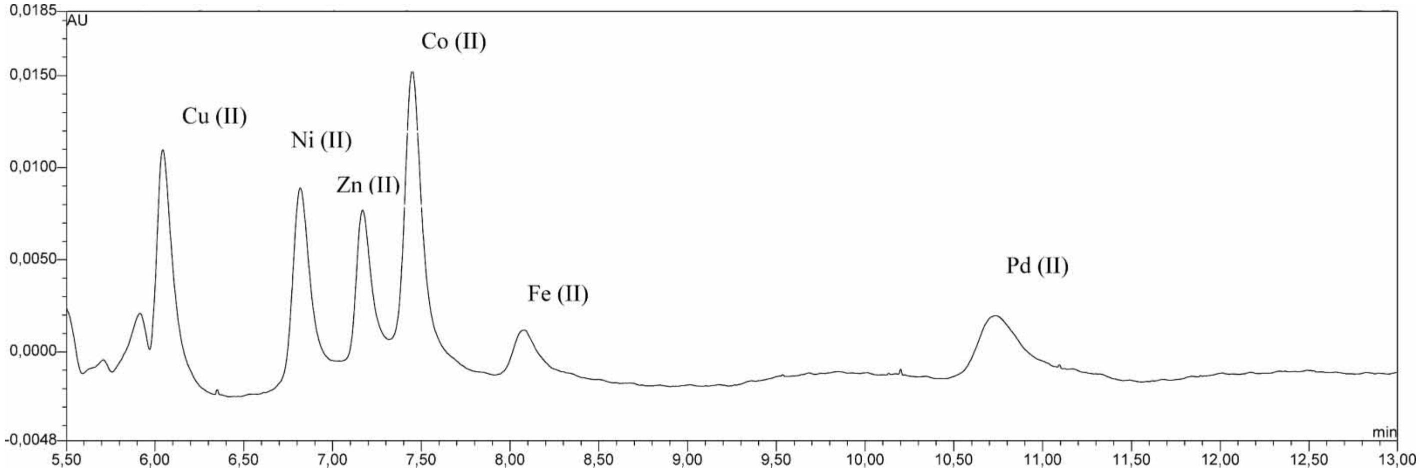

Figure 2. Chromatogram of a heavy metals standard solution. Peaks: Cu(II) (2 ppb), Ni(II) (1 ppb), Zn(II) (100 ppb), Co(II) (1 ppb), Fe(II) (5 ppb), Pd(II) (10 ppb). Loop volume: 5 mL.

Table 1. Calibration curve parameters for Cu(II), Ni(II), Zn(II), Co(II), Fe(II) and Pd(II): slope (m), standard deviation of slope (s_m), intercept (b), standard deviation of intercept (s_b), standard error (s_y), number of data points (n), correlation coefficients (r^2) and investigated range (range)

Element	m	s_m	b	s_b	s_y	n	r^2	Range (ppb)
Cu(II)	1.17E−03	3.8E−05	−6.80E−04	2.0E−04	4.2E−04	9	0.9936	0.2−10
Ni(II)	1.29E−03	1.4E−05	6.82E−05	7.5E−05	1.9E−04	12	0.9989	0.05−10
Zn(II)	1.03E−05	1.1E−07	−8.71E−06	5.2E−05	1.3E−04	12	0.9991	5−1000
Co(II)	2.08E−03	1.0E−05	−4.69E−05	4.8E−05	1.2E−04	12	0.9998	0.05−10
Fe(II)	3.40E−04	9.5E−06	−1.09E−03	2.7E−04	5.1E−04	7	0.9961	2.5−50
Pd(II)	1.62E−04	2.6E−06	−1.12E−04	6.6E−05	9.1E−05	5	0.9992	5−50

Table 2. Limit of detection (LOD) for Cu(II), Ni(II), Zn(II), Co(II), Fe(II), and Pd(II) in method 1 (proposed method), in method 2 (method of Bruno et al.[26]) and in method 3 (method of Bruno et al.[25]).

Element	Method 1 LOD (ppb)	Method 2 LOD (ppb)	Method 3 LOD (ppb)
Cu(II)	1.1	0.5	10
Ni(II)	0.5	0.5	10
Zn(II)	39	1	10
Co(II)	0.18	0.5	10
Fe(II)	4	4	–
Pd(II)	1.7	–	–

calculated R^2 values show a good linearity in the considered ranges. Detection limits (LOD) and quantification limits (LOQ) were estimated for each metal from the parameters of linear regressions[32] (see s_y in Table 1). In Table 2 LOD values obtained with the proposed method and those with previous methods are compared;[25,26] it is possible to observe that hexadecylpyridinium in the PCR and the detection at 540 nm make the method very selective. In fact, while the loop increasing produces a foregone rising of the signal for all analytes due to bigger sample amounts, modifications in PCR determine the Pd(II) detection, a better detection of Co(II), and a worse for Zn(II), and no significant influence for Cu(II), Ni(II), and Fe(II) determination. Unfortunately, these detection conditions do not allow revealing of Fe(III), Cd(II), Mn(II), and Pb(II). It is important to point out that the method which does not detect Fe(III) can be useful too: sometimes, the abundance of this analyte in environmental matrices could make difficult the revelation of the other low abundant metals. Reproducibility (%RSD) of the proposed method, evaluated on three inter-day replicates, is lower than 15% in the ppb linearity range.

CONCLUSIONS

A method allowing separation of Cu(II), Ni(II), Zn(II), Co(II), Fe(II), and Pd(II), in less than 15 minutes by ion chromatography, was developed starting from previous works and studying the absorption properties of PAR complexes. The method of Bruno et al.[25] was improved in order to obtain palladium detection. The increase of injection volume and the different PCR composition were the main changes. Very interesting LOD values at ppb/subppb levels were obtained for considered analytes, with the further advantage to allow palladium detection at ppb level. Moreover, this method exhibits good linearity and reproducibility for these six metals in the ppb ranges. The proposed procedure can be of great interest for environmental monitoring and industrial process check.

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Received October 13, 2006
Accepted November 11, 2006
Manuscript 6966