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Short communication

Capillary electrophoretic determination of cyanide leaching solutions from automobile catalytic converters

M. Aguilar, A. Farran*, V. Martí

Department of Chemical Engineering, ETSEIB, Universitat Politècnica de Catalunya, Diagonal 647, 08028 Barcelona, Spain

Abstract

A capillary electrophoresis (CE) method to determine metal–cyano complexes from leaching solutions of automobile catalytic converters has been developed. The separation and detection conditions have been optimized and analysis times up to 20 min and metal detection limits in the ppb range have been obtained. The CE analysis of leaching solutions from different converters allowed the determination of Fe(II)–, Cu(I)–, Ni(II)–, Pd(II)– and Pt(II)–cyano complexes and NO_3^-. On the other hand, adsorption onto activated carbon is used as a concentration process for precious metal–cyano complexes and as a process of pollutant removal. The adsorption kinetics of the compounds of interest have been studied by means of the developed CE method. The results obtained by CE have been compared with inductively coupled plasma in order to validate this newly developed method. © 1997 Elsevier Science B.V.

Keywords: Automobile catalytic converters; Metals; Metal complexes; Cyanide complexes

1. Introduction

The atmospheric pollution from motor vehicles is an important problem that, in recent years, has been palliated with the incorporation of three-way platinum group metals (PGMs) catalytic converters. Pt and Pd are used to control the emissions of carbon monoxide and hydrocarbons, and Rh is used to control nitrogen oxides.

Depletion and the loss of efficiency are the reasons why the converters turn into a new residue which has to be treated. The industrial recovery of PGMs from the converters can be an economically viable process that would decrease the pollution due to mining processes to obtain PGMs and the cost of the converters in the new vehicles. By the year 2000 it is anticipated that the mass of catalytic converters available for recycling in Europe will be about 4000 tonnes/year [1].

Different pyrometallurgic and hydrometallurgic industrial processes [2] have been developed to recover PGMs from exhausted automobile catalytic converters. An alternative way is a leaching process based on intensive cyanidation steps at high temperature to dissolve PGMs [3–5] followed by adsorption onto activated charcoal to recover them [6]. The activated charcoal adsorption step can be used as a concentration process of precious metals and as a pollutants removal process [7,8]. In any case, an analytical control is needed to study the dissolution and the recovery of PGMs in the leaching process, and to control wastes. At the present, atomic absorption spectrometry (AAS) and emission spectrometry by inductively coupled plasma (ICP) are the two main techniques used to analyze total metals [9].

Converters have a great percentage of metal oxides that constitute the support and the channel

*Corresponding author.

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coating [4,10] and some of them can act as cyanicides in the leaching process, so it will be interesting to have an analytical technique that allows the simultaneous determination of different metals and their speciation as cyano complexes. Some chromatographic methods have been developed to analyze Pd– and Pt–cyano complexes [11–13]. A new approach is to use capillary electrophoresis (CE) that has proven to be effective in the separation and detection of some metal cyanide [14–17] complexes. In the present work, a CE method to analyze Fe(II)–, Cu(I)–, Ni(II)–, Pd(II)– and Pt(II)–cyano complexes and NO_3^- from leaching solutions of automobile catalytic converters and to study the evolution and the final composition of the solutions obtained from the adsorption onto activated charcoal has been developed.

2. Experimental

2.1. Solutions and reagents

NaCN solutions with pH maintained above 11 by using NaOH, to avoid HCN formation, were used to dissolve PGMs.

Stock standard solutions were prepared by dissolving $K_2Pt(CN)_4$, $K_2Pd(CN)_4$ and $K_2Ni(CN)_4$ from Aldrich (Milwakee, WI, USA), $K_4Fe(CN)_6 \cdot 3H_2O$ from Merck (Darmstadt, Germany) and CuCN from Johnson Matthey Chemicals (Karlsruhe, Germany) in an alkaline solution of NaCN. Rh(III) cyanide standard (bellow 100 ppm Rh) was prepared dissolving small weighted amounts of solid $RhCl_3 \cdot 3H_2O$ from Johnson Matthey Chemicals in excess of NaCN (40–50 g NaCN/l) in order to avoid the precipitation of $Rh(CN)_3$ (s).

Activated charcoal was Picagold G210 type purchased from Pica (Vierzon, France).

Analytical grade $Na_2HPO_4 \cdot 2H_2O$, NaCN, NaCl, and tetradecyltrimethylammonium bromide (TTAB) from Merck and tetrabutylammonium bromide (TBAB) from Fluka (Buchs, Switzerland) were used to prepare different buffer solutions with pH 11–12 for the CE system.

The electrolyte and sample solutions were prepared with water deionized with a Milli-Q system Millipore, filtered through a 0.45 μm membrane filter from LIDA (Kenosha, USA).

2.2. Instrumentation

An ISCO (ISCO, Lincoln, NE, USA) Model 3850 integrated capillary electrophoresis system equipped with high voltage up to 30 kV and reversible polarity was used. Samples were introduced by applying a 3.4 kPa vacuum at the detector end of the capillary. Separations were performed at a constant negative voltage with untreated fused-silica capillary 80 cm (60 cm to the detector) in total length with 0.05 mm I.D. Detection was carried out by on-column measurement of UV absorption (ISCO CV^4). Data were collected using commercial software (Varian Star Workstation, Sugar Land, TX, USA) on an IBM-compatible 486 computer.

An ICP-Spectroflame (Spectro, Kleve, Germany) was used to measure the total metal concentrations.

2.3. Catalyst sample description

Two types of automobile monolith converters were tested: virgin and used. The virgin monoliths were rejects from a manufacturer's production line (SEAT) and used monoliths were purchased from Opel-GM. Monolith converter consists of a honeycomb structure of corderite coated with γ-alumina, and impregnated with PGMs. As there is no standard catalyst formulation and use, catalysts contain different amounts of PGMs [10] and other metals and compounds used to promote the catalytic reactions and to stabilize the γ-alumina wash coat respectively.

2.4. Leaching process

Converters were crushed, ground wet and sieved to the desired size. After this the sample was homogenized and dried. Leaching processes were conducted in 100 ml flask without agitation put in 40 l autoclave for 1 h at 140°C. Samples of 5 g of converter were leached with 10–50 ml of alkaline solution (0.01–0.1 *M* NaOH) with NaCN concentration ranging from 2 to 10 g/l. Solids and liquids were separated after leaching by vacuum filtration with a Buchner funnel. After cooling, the mixture of

converter and leaching solution was decanted, centrifuged and filtered before being analysed.

2.5. Adsorption process

The adsorption of Pt–, Pd– and Rh–cyano complexes and other metal cyanide complexes was carried out using batch experiments. A sample of 2 g of activated charcoal was mixed mechanically in special glass stoppered tubes with 10 ml of aqueous solution during desired time (5 to 80 min). Samples were analysed directly by CE and were diluted fivefold with deionized water for ICP analysis.

Table 1
Resolution (Rs) between Pt(II) and Pd(II) cyanides and efficiency (N) for Pd(II) cyanide as a function of TBAB and NaCN added to the buffer

Buffer additives		Experimental values	
[TBAB] (mM)	[NaCN] (mM)	R_s (n=3)	N_{Pd} (n=3)
0	3	1.06±0.01	141 000±4000
0.2	1	1.29±0.02	138 000±6000
0.2	5	1.32±0.01	140 000±1000
0.6	0	1.97±0.01	128 000±2000
0.6	3	1.77±0.02	130 000±6000
0.6	6	1.77±0.02	134 000± 900
1	1	2.20±0.04	117 000±7000
1	5	2.20±0.01	122 000±5000
1.2	3	2.43±0.02	126 000±5000

3. Results and discussion

Speciation of PGMs in solution is very important when defining the recovery steps of the PGMs. The intensive cyanidation process is done at 140°C and the theoretical species formed under these conditions are $Pt(CN)_4^{2-}$ and $Pd(CN)_4^{2-}$ [18]. There are not sufficient equilibrium data of formation of Rh cyanide complexes to study its speciation, but several references point to the formation of $Rh(CN)_6^{3-}$ in excess of CN^- at 25°C [3,19].

Standard solutions of Pd(II)–, Pt(II)– and Rh(III)–cyano complexes were used to optimize resolution and detection of PGMs in the CE system.

The use of a Na_2HPO_4 buffer at pH 11 with several TTAB concentrations to adjust electroosmotic flow, showed that the Pd(II)– and Pt(II)–cyano complexes elute at the same time, and that the Rh(III)–cyano complex cannot be detected.

The first problem was solved by using a short-chain quaternary ammonium salt such as TBAB to differentiate between the mobilities of both cyano complexes by ion-pairing formation [20], and by adding NaCN to the buffer to favour the formation of $Pd(CN)_5^{3-}$ [Pt(II) cannot form a similar compound [19]]. Different TBAB and NaCN concentrations were tested and the best results were obtained for 1.2 mM TBAB and 3 mM NaCN (see Table 1).

The second problem could not be solved. The mobility of the $Rh(CN)_6^{3-}$ complex would be similar to the mobility of other metal– cyano complexes because of its charge/mass ratio, and it must be easily detected. So, the fact that Rh(III)–cyano complex has not been detected can not be explained at the moment and additional experiments are being carried out at the present to study the problem.

Limits of detection (LODs) for different metals were determined by using the optimized conditions: a Na_2HPO_4 (20 mM), NaCl (100 mM), NaCN (3 mM), TBAB (1.2 mM) and TTAB (40 μM) buffer solution at pH 11, a negative voltage of 15 kV and a detection wavelength of 208 nm. Two different sample matrices to simulate the process (NaCN and NaOH) and the waste (NaOH, pH 11) solutions were used and the LODs for different injection times are tabulated in Table 2, where it can be observed that for a constant injection time, LODs decreases with the matrix conductivity due to the stacking effect.

The optimized CE method has been applied to the analysis of solutions obtained from the intensive cyanide leaching of virgin and used automobile monolith converters (140°C for 1 h). Results indicated the presence of the cyano complexes $Pt(CN)_4^{2-}$, $Pd(CN)_4^{2-}$, $Fe(CN)_6^{4-}$, $Ni(CN)_4^{2-}$, $Cu(CN)_3^{2-}$ and NO_3^- (see Fig. 1), the last one being a depletion product of CN^- due to the high temperature used in the cyanide leaching process [21].

ICP semi-quantitative analysis of the same samples shown the presence of Pt, Pd, Fe, Ni, Cu, Rh, Zn, Al, Ba and Mg, that agrees with the matrix composition [3,10]. The remainder metals and no metals detected only by ICP, either do not form cyano complexes (Al and Ba) [19] or form weak and undetectable cyano complexes (Zn) [22]. On the

Table 2
LODs for metal–cyano complexes (ppb metal) as a function of matrices and injection time

Conditions		LOD (ppb)					
Matrix	t_{inj}(s)	Cu(I)	NO_3^-	Ni(II)	Pd(II)	Pt(II)	Fe(II)
NaOH pH=11	100	11	23	60	53	18	10
NaOH pH=11	50	38	89	165	169	50	33
NaCN 2000 (1/5)	50	41	103	242	218	70	40
NaCN 2000 (1/5)	30	67	165	285	268	87	64

other hand, though CE can not detect Rh(III) complex, is capable to detect NO_3^-.

Adsorption onto activated charcoal has been tested as a method to recover the PGMs from the leach solutions as well as a method to remove cyanide pollutants.

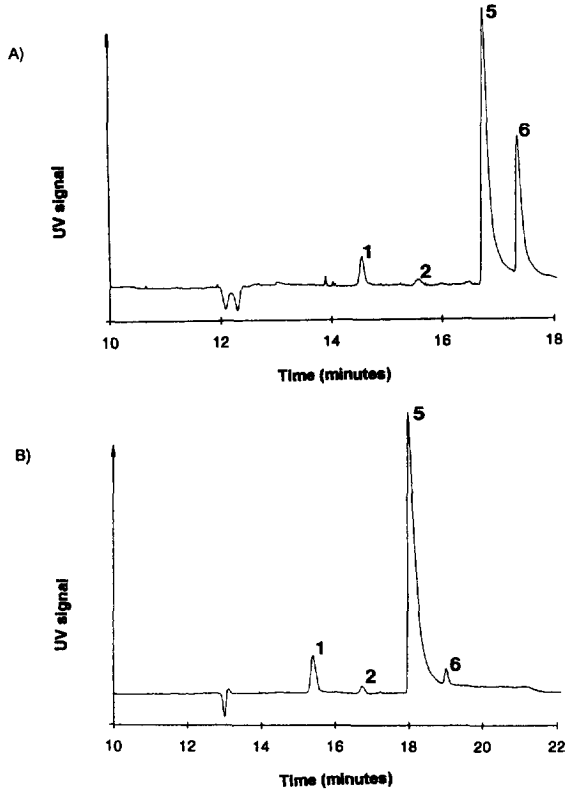

Fig. 1. Electropherograms of automotive converter leaching solutions: (A) Sample M2 (B) Sample M1 (See Table 3 legend). 1, $Cu(CN)_3^{2-}$; 2, NO_3^-; 5, $Pt(CN)_4^{2-}$; 6, $Fe(CN)_6^{4-}$. Analytical conditions: running buffer Na_2HPO_4 20 m*M*, NaCl 100 m*M*, NaCN 3 m*M*, TBAB 1.2 m*M*, TTAB 40 μ*M* at pH 11. Applied voltage: −15 kV. Detection wavelength: 208 nm.

A mixture of leaching solutions was adsorbed onto activated charcoal in a batch process using several rotatory tubes. The sampling of the adsorbed solution with time and the analysis of metals by CE and ICP gave the electropherograms shown in Fig. 2 and the kinetics in % of adsorption shown in Fig. 3 (each point is the average value of two samples).

In both figures it could be seen that Pt(II), Pd(II)

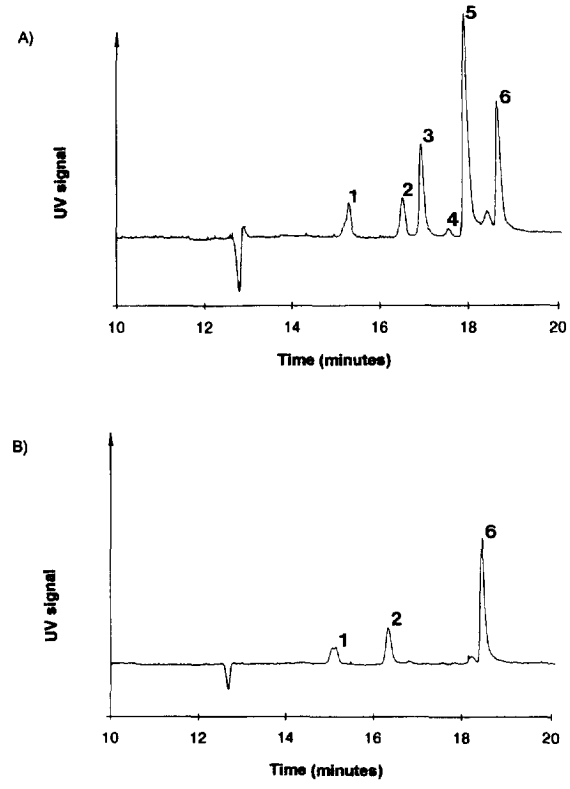

Fig. 2. Electropherograms of adsorbed solutions: (A) Sample A1 (B) Sample A2 (See Table 3 legend). 1, $Cu(CN)_3^{2-}$; 2, NO_3^-; 3, $Ni(CN)_4^{2}$; 4, $Pd(CN)_4^{2-}$; 5, $Pt(CN)_4^{2-}$; 6, $Fe(CN)_6^{4-}$. Analytical conditions as in Fig. 1.

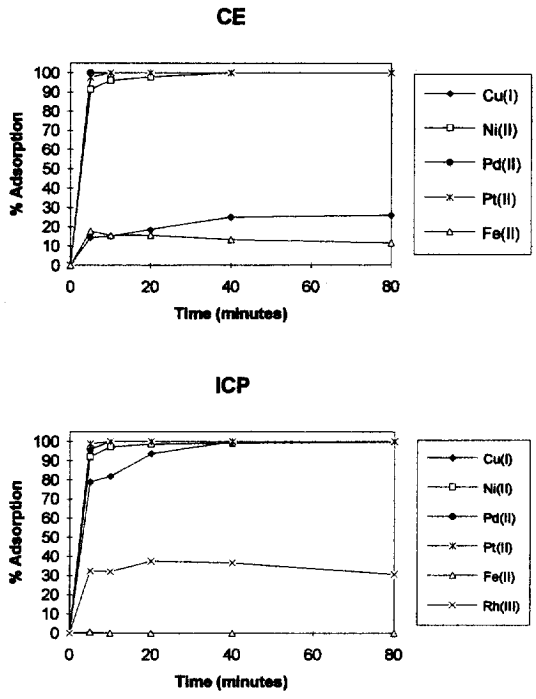

Fig. 3. Kinetics of adsorption for cyano complexes analysed by CE and ICP.

and Ni(II) cyanides were selectively adsorbed onto carbon in a short time while Fe(II) and Rh(III) cyanides and NO_3^- show much lower adsorption. Such behaviour invalidates the adsorption onto activated charcoal as an effective method to remove common cyanides such as $Fe(CN)_4^{2-}$, but it opens the possibility of a way to separate selectively the Rh(III) cyanide from the Pt(II) and Pd(II) cyanides. The selective adsorption of Pd(II), Pt(II) and Ni(II) cyanides can be bound to their chemical structure, that is square planar for Pd(II), Pt(II) and Ni(II), and octahedral for Fe(II) and Rh(III) [3,19].

By comparing the metal concentrations obtained by CE and ICP in the case of leaching and adsorbed samples in Table 3 it could be seen that results are similar though the curves of percentage of adsorption for Cu(I) and Fe(II) cyanides are very different.

In the case of Cu(I) this could be due to five-fold dilution factor of sample used to measure by ICP (that gave concentrations similar to LODs) and in the case of Fe(II) the difference was due to the low precision of CE concentration (2–10% R.S.D.) compared with ICP (1–2% R.S.D.).

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Table 3
Comparison of metal–cyano complex concentrations (ppm metal) analyzed by CE and ICP (three measurements)

	A1		A2		M1		M2	
	CE	ICP	CE	ICP	CE	ICP	CE	ICP
Pt(II)	47±1	45.9±0.2	ND	ND	130±10	128±2	462±9	405±9
Pd(II)	0.99±0.08	1.19±0.02	ND	ND	ND	0.65±0.01	ND	0.066±0.003
Rh(III)	*	5.63±0.02	*	3.91±0.06	*	23.51±0.09	*	45.6±0.8
Cu(I)	0.37±0.08	0.331±0.004	0.31±0.01	ND	0.43±0.02	0.728±0.002	2.7±0.1	0.69±0.02
Fe(II)	4.1±0.1	4.0±0.1	4.2±0.1	4.43±0.06	9.9±0.9	9.1±0.2	1.4±0.1	1.62±0.04
Ni(II)	15.7±0.8	13.3±0.2	ND	ND	ND	0.414±0.001	ND	0.53±0.02
NO_3^-	4±1	*	4.8±0.3	*	ND	*	3.4±0.1	*

A1, Mixture of leaching solution used in activated charcoal adsorption experiment.
A2, Sample A after 80 min in contact with activated charcoal (see conditions in text).
M1, Leaching solution from spent converter (10 g/l NaCN, 0.1 *M* NaOH, ratio solid to solution 1/5, size <325 mesh).
M2, Leaching solution from virgin converter (same conditions as C).
ND=Not detected by the technique. *=Not detectable by the technique.

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