ELSEVIER

Journal of Chromatography A, 871 (2000) 217–226

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Separation of some platinum group metal chelates with 8-hydroxyquinoline by various high-performance liquid chromatographic methods

J.M. Sánchez, O. Obrezkov[1], V. Salvadó*

Chemistry Department, University of Girona, Campus Montilivi s/n, 17071 Girona, Spain

Abstract

Different HPLC methodologies are employed to evaluate the separation and determination of some platinum metals (Pt, Pd, Ir and Rh) after the formation of 8-hydroxyquinolate chelates. With the aim of reducing the number of steps in treating the samples, the method developed did not include the elimination of excess chelating reagent before the analysis of metal chelates. Reversed-phase (RP), non-aqueous reversed-phase (NARP) and normal-phase (NP) HPLC are compared. The RP-HPLC method only permits the quantitative separation of Rh and Pd from the excess reagent. A silica column can be used to separate Ir and Rh by NP-HPLC. The NARP-HPLC method allows for the effective separation of the four elements tested, but the high detection limit (90 ng) for platinum and the peak width do not favour its application for quantitative measurement. Platinum group metals can be quantitatively separated and determined by NP-HPLC using a cyano column in less than 15 min. The broad linear range of all the elements (between 1 and 500 ng) is superior to that which has been previously reported and the detection limits (1.0 ng for Pt, 0.3 ng for Pd, 1.0 ng for Ir and 0.3 ng for Rh) are slightly lower.

Keywords: Mobile phase composition; Hydroxyquinolines; Metal chelates; Platinum; Rhodium; Palladium; Iridium

1. Introduction

The use of chromatographic methods for the determination of samples containing mixtures of platinum group metals (PGMs) has increased over the last two decades. High-performance liquid chromatography (HPLC), due to its high level of sensibility, has established itself as the most widely used of these techniques.

PGMs can be separated and determined by HPLC either as organometallic compounds or as chelates. The first possibility does not allow for effective analysis, but the second can be quantitatively analysed by HPLC with a high level of precision given that the structure and properties of chelates are similar to organic compounds [1]. The most suitable ligands for the PGM chelate formation for HPLC analysis are *N*-heterocyclic azodyes [1,2] and 8-hydroxyquinoline (HOx) [1–6].

Most studies until now have used normal-phase (NP) HPLC methods [4–6] for the separation and determination of PGM oxinates. However, the use of a cyano column has not been previously reported for the separation of PGMs. To the best of our knowledge, only one study has employed reversed-phase (RP) HPLC methods [3]. The main drawback of

*Corresponding author. Tel.: +34-972-418-262; fax: +34-972-418-150.

E-mail address: victoria@fc.udg.es (V. Salvadó)

[1]On leave from the Analytical Chemistry Department, University of Moscow, Russia.

0021-9673/00/$ – see front matter
PII: S0021-9673(99)01014-6

PGM oxinates is that an excess of HOx is needed to obtain a quantitative formation of metal chelates when they are analysed by HPLC, and the excess is extracted by the organic solvents used in the extraction step. The analytical wavelength for the determination of metal chelates was 254 nm in these earlier studies. The excess of HOx produces a high interference at this wavelength reaching a maximum of absorbance at 318 nm. This makes it necessary to eliminate the excess reagent by a re-extraction with NaOH.

The mobile phases used in these studies were binary phases containing mixtures of chloroform or methylene chloride with strong eluents, such as THF or 2-propanol. The separation of all PGM oxinates was obtained through a mobile phase of methylene chloride–2-propanol (97:3, v/v) [4].

The aim of this study was to find the best, NP or RP-HPLC method for the separation and determination of PGMs (Pt, Pd, Ir and Rh), without the need to eliminate the excess reagent. We also wanted to establish the precise amount of excess reagent needed for the optimum sensitivity in HPLC analysis.

2. Experimental

2.1. Apparatus

The chromatographic experiments were performed on a Shimadzu chromatograph equipped with two pumps (LC-9A) and a UV–visible spectrophotometric detector (SPD-6AU). Samples were injected by means of a Rheodyne 7725i loop injector.

Two normal-phase columns and one reversed-phase column were used in this study. The C_{18} RP column was Spherisorb ODS-2 (150×4.6 mm, average particle diameter: 5 μm) (Teknokroma, Spain). The NP columns were Silasorb-600 (250×3 mm, average particle diameter: 10 μm) (BioChemMac, Russia) and Nucleosil 100 CN (150×4.6 mm, average particle diameter: 5 μm) (Teknokroma, Spain).

2.2. Reagents

Working solutions of PGMs were obtained by the dilution of atomic absorption standard solutions of approximately 1000 mg l^{-1} of metal (Aldrich, USA) with ultra-pure water (Milli-Qplus, Millipore). The chelating reagent was HOx (PA, Panreac, Spain).

Acetonitrile (ACN), tetrahydrofuran (THF), methanol, ethanol, butanol, chloroform and dichloromethane were all HPLC grade (Carlo Erba, Italy) and they were filtrated in 0.45-μm filters and degassed for 10 min in an ultrasonic bath.

All other chemicals were of analytical grade.

3. Results and discussion

3.1. Preparation of sample solutions

In previous studies [3–6], the PGM oxinates were prepared as follows: solid 8-hydroxyquinoline, or a solution in acetic acid or propanol [6], was mixed with a known volume of metal solution containing 1–200 μg of metal, pH 4.8 acetate buffer and diluted to a known volume. The mixture was heated for 2 h in a water bath at 90°C [6], then cooled and mixed with chloroform.

The amount of HOx added for the formation of the complex was maintained at 30 mg in all of these studies. The evaluation of the effect of excess reagent has shown that it is highly dependent on the PGM ion (Table 1). The more reactive metals (Pd and Rh) do not need a great excess of reagent as the determination has the same sensitivity with both 6 mg and 30 mg of excess HOx. On the other hand, for Pt and Ir the sensitivity is 2.4 and 3.9 times higher with 30 mg of HOx, respectively. We chose Ir to evaluate the precise excess of reagent needed to obtain a constant area as this element showed the

Table 1
Increase in the sensibility of the determination of different PGMs when the excess of 8-hydroxyquinoline added for the formation of the chelate is increased (S_x indicates the sensitivity of the complex with x mg of excess reagent)[a]

Flow-rate (ml min^{-1})	S_{30}/S_6			
	Ir	Rh	Pd	Pt
1.0	3.79±0.12	1.02±0.10	1.04±0.06	2.39±0.10
0.5	3.97±0.08	1.06±0.06	1.05±0.05	2.44±0.08

[a] Experimental conditions: Spherisorb ODS-2 column, THF–chloroform (30:70, v/v). Three replicates.

greatest increase. We found that a minimum of 30 mg of HOx is needed to obtain a constant amount of complex formed by the less reactive metal (Ir).

The solvent chosen for the extraction and preconcentration of the metal oxinates was dependent upon the kind of column employed. Chloroform was the solvent used in normal- and non-aqueous reversed-phase (NARP) chromatography and 1-butanol was used in the reversed phase. Previous studies [4,6] have shown that the extraction of PGM oxinates is obtained in only 2 min when chloroform is used as the solvent. The evaluation of the extraction time for 1-butanol has indicated that the formation of 100% of the metal complex is obtained in only 1 min. An increase in the contact time, however, produces a decrease in the peak area corresponding to the excess HOx without a change occurring in the sensitivity of the palladium oxinate analysed. The effect of the extraction time with 1-butanol on the sensitivity of excess of HOx and palladium oxinate has been evaluated. The lowest sensitivity for the excess of reagent without changes in the peak of the chelates has been obtained for an extraction time of 40 min.

In the case of UV detection, the excess of reagent must be previously eliminated in order to avoid interference in this region. The formation of a second maximum absorption band at 410–435 nm [6] permits the analysis of PGM oxinates in the visible range without the elimination of excess HOx (Fig. 1).

The results obtained show that the chromatographic determination of the PGM oxinates is possible without the elimination of excess HOx by measuring within the visible range of the spectrum (435 nm).

3.2. Optimisation of the chromatographic conditions

The following parameters were used to describe the chromatographic behaviour of chelates: the retention volume (V'_R) corrected for the dead volume of the column, the capacity factor (k), the separation factor (α) and the resolution (R_s) of two adjacent peaks.

3.2.1. Reversed-phase chromatography

Chloroform has been used as the solvent for PGM oxinates in an RP-HPLC method described in the literature [3]. In this study, 1-butanol was selected as an alternative solvent for the extraction of chelates due to its greater compatibility with reversed-phase columns. This compound presented several narrow peaks in the chromatogram in all the mobile phases tested, but these peaks were always at the front and did not disturb the determination of the chelates.

The composition of the mobile phase was optimised by varying the percentage of ACN or THF with water. In all cases, the elution order of the chelates, which correlates with the decrease in electronegativity (1.55–1.45–1.44–1.39), was Ir< Rh<Pt<Pd. The peak corresponding to the excess of HOx showed the same retention time as Pt oxinate although their separation in the 15 cm column was difficult. The separation of both peaks with a lower t_R for the metal chelate was made possible by the increase of the column length to 25 cm.

Mobile phases based on ACN had a lower eluting power for PGM oxinates. The peaks were wider and we managed to separate the compound that was most retained, palladium oxinate, from the rest of the compounds even in 100% ACN mobile phase (Fig. 2). The peaks corresponding to Ir and Rh oxinates were separated by increasing the percentage of water in the mobile phase. Very poor resolution ($R_s<0.5$), however, was obtained because the low eluting power of these mobile phases produces wide peaks.

The use of THF, a stronger eluent, improves the separation of Ir, Rh and Pd oxinates. The binary mobile phase containing THF and water was modified by the addition of different salts (1 m*M* perchlorate or acetate) at different pH values. The retention time of the chelates did not change with the addition of salt. The sensitivity was lower, however, when the mobile phase contained 1 m*M* of perchlorate and no significant differences were observed between ultra-pure water and acetate buffer. Increasing the pH resulted in narrower peaks and increased resolution. The highest resolution values were obtained with a mobile phase of THF–1 m*M* acetate at pH 7.4 (30:70, v/v) (Table 2). In these conditions only Rh and Pd could be quantitatively separated from the excess reagent.

Iridium oxinate solutions presented two peaks in all the mobile phases that were tested. The first peak appeared close to the front whereas the second had a

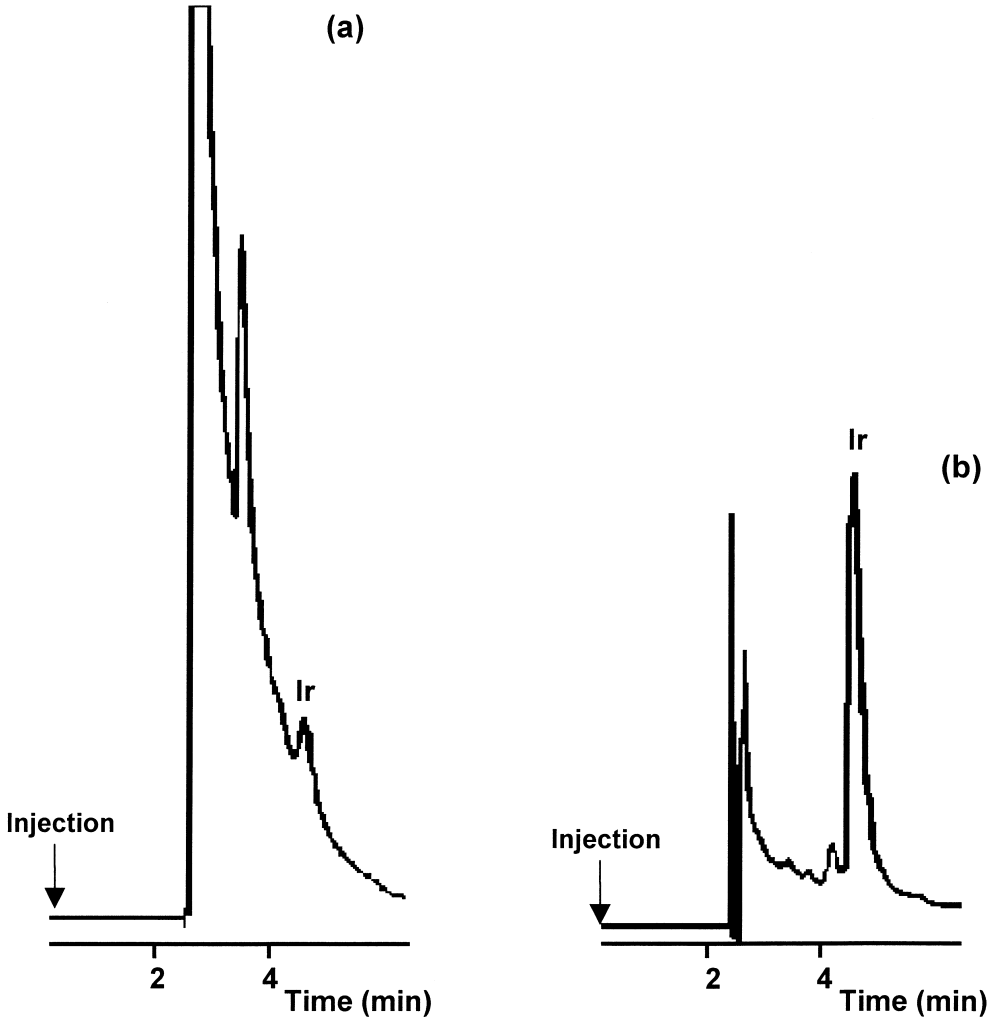

Fig. 1. Liquid chromatograms obtained for Ir (100 ng) at different wavelengths: (a) 254 nm; (b) 435 nm. Chromatographic conditions: Silasorb 600 column, chloroform–THF (60:40, v/v), 20 μl injection, 1.0 ml min^{-1}.

retention time higher than that corresponding to the Rh oxinate peak. The presence of more than one peak may be explained by the spontaneous reduction of part of the Ir(IV) leading to the formation of Ir(III) oxinate. This redox process, which depends on pH and time in HCl media, has been described in an earlier study [7].

The results showed that the chelates of Ir and Pt are not stable in 1-butanol. A change in the colour of their solutions and in the sensitivity of the chelate peaks was observed 5 min after their preparation. The decrease in the peak area over time detected for these two compounds suggests the possibility of changes in the speciation of the solution. In the case of Ir, new peaks appeared 1 day after the preparation of the sample.

3.2.2. Normal-phase chromatography

Chloroform–THF mixtures are not sufficiently selective for the separation of platinum oxinates by means of isocratic elution [3,4]. For this reason, the use of binary phases containing mixtures of chloroform or methylene chloride with stronger eluents, such as 2-propanol, have given better results in the

Fig. 2. Chromatogram obtained for a Pd sample (202 ng) with 100% ACN mobile phase in reversed-phase HPLC. Chromatographic conditions: 20 μl injection, 1.0 ml min^{-1}.

separation of all PGM after the elimination of excess HOx [4]. However, a weaker elution mobile phase is required when there is an excess of HOx in the samples.

The elution order of metal oxinates in NP-HPLC is Pt<Pd<Os<Ru<Ir<Rh [4]. Excess HOx was not retained as long as PGM oxinates and there was a wide peak close to the front of the chromatogram. Only the less retained compounds, Ir and Rh (Table 3), could be quantitatively separated ($R_s \geq 1.5$) in the presence of HOx by this technique. Pd and Pt chelates have not been analysed with silica columns as their peaks cannot be separated from the oxine peak. The effect of different polar additives on the elution capacity of the mobile phase has been studied (Fig. 3). This figure shows the linear relationship of the polar additive effect with polarity.

Table 2
Resolution values obtained for the separation of front peak/Rh, Rh/HOx and HOx/Pd using a reversed-phase column (Spherisorb ODS 2)[a]

Aqueous solution	pH	R_s		
		Front/Rh	Rh/HOx	HOx/Pd
Water		0.7	1.3	0.8
Perchlorate 1 m*M*	5.6	0.7	2.1	1.6
Acetate 1 m*M*	3	0.8	0.6	1.0
	4	1.4	0.9	1.4
	7.4	1.8	1.3	1.8

[a] Experimental conditions: THF–aqueous solution (30:70), 1.0 ml min^{-1}, $\lambda = 435$ nm.

The quantitative measurements of Ir and Rh in the presence of HOx gave better results for Ir than those obtained by Alimarin et al. [4] decreasing its detection limit to 3 ng and increasing the linear range from 5 ng to 500 ng when the composition of the mobile phase is chloroform–THF (70:30) and 20 μl of the sample are injected.

3.2.3. Non-aqueous reversed-phase chromatography

The use of an RP column with mixtures of two organic solvents can sometimes be used when the sample is not soluble in aqueous solution [8]. In this case, the impossibility of separating the less retained chelates in NP-HPLC in the presence of HOx, and the poor stability of some of the PGM chelates in usual reversed-phase solvents has improved the use of NARP-HPLC. The results obtained (Table 4) indicate that the separation of the four elements evaluated is possible with the use of a mobile phase composed of chloroform (polarity index, $P' = 4.1$) as a poor solvent, and THF ($P' = 4.0$) as a strong solvent. The elution of the metal oxinates in these conditions follows the same order as with NP-HPLC (HOx<Pt<Pd<Ir<Rh). The effective separation of all the metal oxinates and HOx ($R_s \geq 1.5$) is obtained with a mobile phase of chloroform–THF (95:5, v/v). The capacity factor of Rh oxinate, however, is very high ($k = 14.34$) in this mixture. The use of a gradient elution permitted the analysis of the four elements in

Table 3
Dependence of the chromatographic parameters of the 8-hydroxyquinolates of Ir and Rh on the nature and composition of the mobile phase in NP-HPLC[a]

Polar additive	Metal	Content of polar additive (%, v/v)																	
		1				2				3				4				5			
		V'_R	k	α	R_s	V'_R	k	α	R_s	V'_R	k	α	R_s	V'_R	k	α	R_s	V'_R	k	α	R_s
MeOH	Ir	3.03	1.57	–	–	1.67	0.84	–	–	0.79	0.41	–	–	0.52	0.26	–	–	0.48	0.24	–	–
	Rh	4.35	2.26	1.44	2.73	2.33	1.20	1.42	1.81	1.49	0.76	1.87	0.97	1.05	0.54	2.03	0.61	0.84	0.43	1.74	0.41
EtOH	Ir	4.00	2.02	–	–	2.08	1.07	–	–	1.22	0.66	–	–	0.93	0.48	–	–	0.70	0.36	–	–
	Rh	6.25	3.10	1.54	3.33	2.94	1.52	1.42	2.41	1.81	0.93	1.40	2.00	1.28	0.66	1.37	1.31	0.94	0.48	1.35	1.32
BuOH	Ir	6.25	3.10	–	–	4.17	2.12	–	–					2.33	1.26	–	–				
	Rh	9.09	4.70	1.52	2.70	6.25	3.20	1.51	2.35					3.70	1.88	1.48	1.91				
		5				10				20				30				40			
		V'_R	k	α	R_s	V'_R	k	α	R_s	V'_R	k	α	R_s	V'_R	k	α	R_s	V'_R	k	α	R_s
THF	Ir	6.67	3.45	–	–	4.76	2.38	–	–	2.78	1.43	–	–	2.17	1.12	–	–	1.92	0.99	–	–
	Rh	10.0	5.23	1.52	2.82	7.14	3.56	1.50	2.43	4.00	2.06	1.44	1.86	3.03	1.56	1.39	1.67	2.63	1.35	1.36	1.35

[a] Experimental conditions: chloroform–polar additive, Silasorb 600 column, 1.0 ml min^{-1}, λ=435 nm.

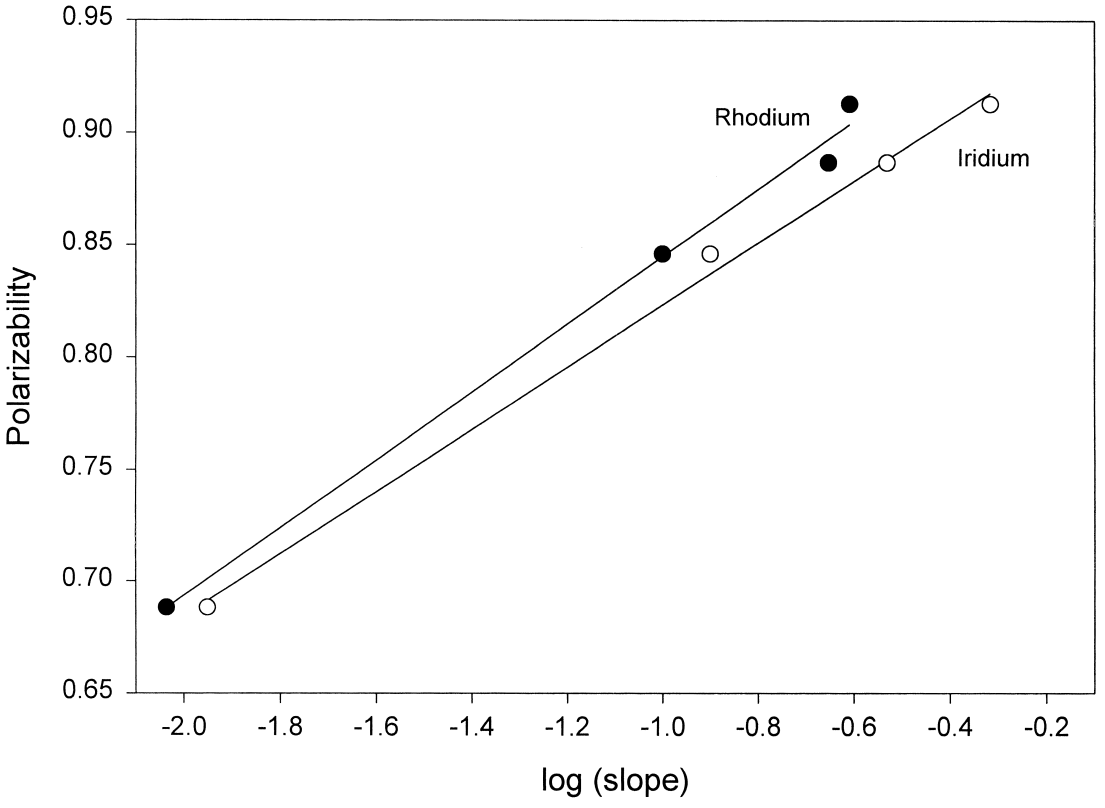

Fig. 3. Relationship between the polarizability of the added polar component and the slope obtained from the calculation of the inverse of the adjusted volume ($1/V'_R$) with respect to the content of the mentioned component.

Table 4
Dependence of the chromatographic parameters of the 8-hydroxyquinolates of Pt, Pd, Ir and Rh on the composition of the binary mobile phase of chloroform–THF in NARP-HPLC[a]

Element	Content of THF (%, v/v)																			
	5				10				20				30				40			
	V'_R	k	α	R_s	V'_R	k	α	R_s	V'_R	k	α	R_s	V'_R	k	α	R_s	V'_R	k	α	R_s
HOx	0.42	0.25	–	–	0.32	0.18	–	–	0.27	0.09	–	–	0.23	0.07	–	–	0.20	0.06	–	–
Pt	1.32	0.84	3.13	1.75	0.65	0.40	2.04	0.51	0.28	0.22	1.25	0.23	0.34	0.16	1.23	0.17	0.21	0.07	1.04	0.02
Pd	2.50	1.61	1.90	2.28	1.12	0.71	1.73	1.58	0.49	0.26	1.73	1.16	0.45	0.23	1.33	0.40	0.32	0.15	1.56	0.40
Ir	7.69	4.96	3.06	2.07	2.78	1.76	2.44	2.44	1.15	0.69	2.35	2.54	0.61	0.34	1.37	0.81	0.44	0.23	1.38	0.52
Rh	20.0	14.34	2.88	2.80	4.76	3.06	1.73	1.61	1.69	1.03	1.47	1.37	0.92	0.54	1.50	1.31	0.63	0.35	1.43	0.74

[a] Experimental conditions: Spherisorb ODS-2 column, 1.0 ml min^{-1}, $\lambda = 435$ nm.

less than 20 min (Fig. 4). The mobile phase consisted of the following chloroform–THF gradients: time 0–5 min, 98:2; time 5–8 min, 90:10; time 8–9 min, 95:5; time 9–12 min, 90:10; time 12–30 min, 85:15. The very high detection limit for Pt (60 ng for 20 μl of injected volume) and the wide peaks are the main disadvantages of this method.

We have observed the presence of a predominant peak and some other additional peaks in analysing Rh and Ir oxinates by NARP-HPLC when the content of THF in the mobile phase was higher than 20% (v/v). Only one peak for each of the PGM oxinates, however, has been observed in a previous study using chloroform as the extractant [4] with NP silica columns. These peaks are associated with the ML_2 complexes for Pd and Pt, and ML_3 for Ir and Rh. In agreement with our results, a thin-layer chromatographic (TLC) study showed the presence of different oxinates for Rh [9]. This finding has been explained by the formation of the monochelate and the *cis*- and *trans*-isomers of the trischelate with HOx as the initial solutions of these compounds form different chloro- and aqua-chloro complexes in the aqueous solutions.

A decrease in the area of all the peaks, with the presence of only one peak in the chromatogram has been observed when the solutions were treated with NaOH to eliminate excess reagent. This effect would explain the formation of only one peak in Alimarin's study [4].

3.2.4. Normal-phase chromatography with a cyano column

A cyano column has not previously been used for the HPLC of PGMs. The elution of the compounds in NP with a cyano column is usually faster than with a silica column. Furthermore, a cyano column equilibrates faster than a silica column and is not affected by the presence of traces of water. The lower retention of the cyano column permits the use of weaker mobile phases such as binary mixtures of hexane and chloroform or dichloromethane ($P' = 3.5$). The eluting power of the mobile phase is controlled by the polar additive content. These characteristics of the cyano columns and the results previously obtained with RP and NP-HPLC indicate the possibility of obtaining good separation and high resolution with these kind of columns.

The results obtained with the cyano column showed sharp Gaussian peaks for all studied platinum metals, and good separation can be obtained for all the chelates in presence of excess reagent (Table 5). The increase in the polar additive concentration, chloroform or dichloromethane, in the mobile phases produced a decrease in the retention time of all the chelates and the peaks became narrower. However, the resolution of neighbouring peaks deteriorated.

The mixture of hexane–dichloromethane showed a low selectivity for the PGM. The peak of the most retained element (Rh) appeared at 23.4 min with a peak width at half height (w_h) of 274 s in 100% dichloromethane. The mobile phase of hexane–chloroform gave the best results, but it was not possible to separate and determine all the studied elements by isocratic elution. The peaks of all the ions tested, however, can be well separated ($R_s \geq 1.5$) using a gradient elution of hexane–chloroform.

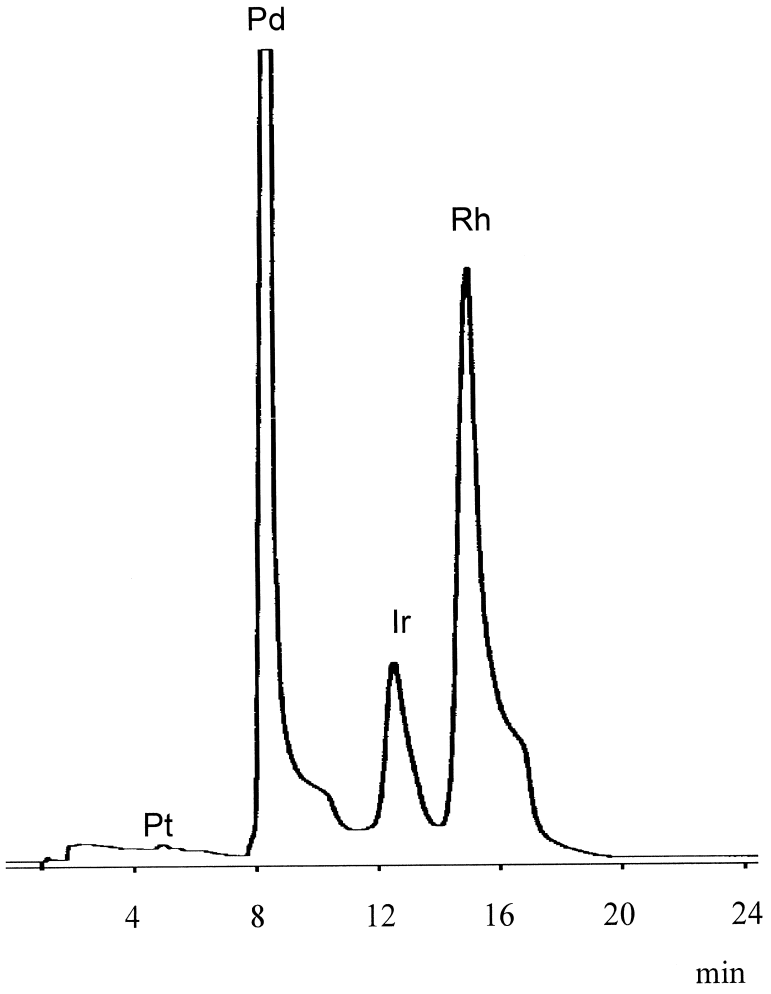

Fig. 4. Chromatogram obtained in the gradient separation of a mixture containing Pt (98 ng), Pd (101 ng), Ir (100 ng) and Rh (102 ng). Chromatographic conditions: Spherisorb ODS-2 column, 20 μl injection, 1.0 ml min^{-1}.

3.3. Retention mechanism

The slope of the plots of log k vs. log X_s, where X_s is the mole fraction of the polar component of the binary mobile phase, indicates the number of bonds formed by the chelates with the adsorbent groups in the columns. Our results gave values of 0.6 bonds for Ir and 0.7 bonds for Rh in a Silasorb 600 column. When a Spherisorb ODS-2 column was used, the number of bonds obtained ranged from 0.7 in the case of HOx to 1.8 for Rh. Finally, when a Nucleosil 100 CN column was used, the number of bonds ranged from 1.7 for HOx to 4.2 for Rh. These findings, which have been confirmed experimentally, lead us to conclude that the chelates should be eluted in the order HOx<Pt<Pd<Ir<Rh for the NP and NARP-HPLC.

3.4. Linear ranges and detection limits

The hexane–chloroform mobile phase with the Nucleosil 100 CN column was selected in order to develop a procedure for simultaneous determination of Pt, Pd, Ir and Rh. The calibration range and

Table 5
Dependence of the chromatographic parameters of the 8-hydroxyquinolates of Pt, Pd, Ir and Rh on the nature and composition of the binary mobile phase with cyano column[a]

Mobile phase	Element	Content of polar additive in the mobile phase (%, v/v)																			
		30				40				60				80				100			
		V'_R	k	α	R_s	V'_R	k	α	R_s	V'_R	k	α	R_s	V'_R	k	α	R_s	V'_R	k	α	R_s
$CHCl_3$–hexane	HOx		0.44	–	–		0.32	–	–		0.18	–	–		0.09	–	–		0.04	–	–
	Pt		2.89	6.63	7.88		1.48	4.55	13.86		0.41	2.34	1.20		0.17	1.86	0.25		0.05	0.84	0.01
	Pd		3.51	1.21	1.88		1.59	1.07	0.67		0.54	1.30	0.84		0.22	1.32	0.32		0.07	1.58	0.29
	Ir		–	–	–		–	–	–		4.25	7.91	8.88		1.28	5.88	6.40		0.53	7.42	3.50
	Rh		–	–	–		–	–	–		5.79	1.36	1.80		1.90	1.48	2.08		0.71	1.35	1.36
CH_2Cl_2–hexane	HOx										0.35	–	–		0.34	–	–		0.48	–	–
	Pt										2.79	8.05	7.75		1.20	3.52	4.86		0.60	0.80	0.51
	Pd										5.34	1.92	2.67		2.30	1.92	2.95		0.88	1.58	2.10
	Ir										6.36	1.19	1.52		2.51	1.09	0.58		1.08	1.23	0.62
	Rh										–	–	–		–	–	–		10.7	9.94	2.10

[a] Experimental conditions: Nucleosil 100 CN column, 1.0 ml min^{-1}, $\lambda = 435$ nm.

detection limit, calculated for a signal/noise ratio of 3, are given in Table 6. When HOx is used as a reagent, calibration graphs are linear over a wider concentration range than that previously reported in the literature [4]. Furthermore, the detection limits obtained fall within the same range.

4. Conclusions

The separation of Pt, Pd, Ir and Rh by complex formation using 8-hydroxyquinoline has been applied to the quantitative determination of these metal chelates without the elimination of excess reagent. The different methodologies evaluated (RP-, NARP- and NP-HPLC) indicate that only the use of NP-HPLC with cyano columns permits the separation and determination of the four elements in a sample with a broad linear range. This range is higher than previously reported using the same reagent and furthermore manages to avoid the prior elimination of excess reagent. The detection limit found is at the same level as that reported by other studies.

Table 6
Calibration parameters and detection limits for the simultaneous determination of PGMs by NP-HPLC with a cyano column

Element	Slope[a] (×1000)	Calibration range (ng)	Detection limit (ng)
Pt	0.408±0.005	3–500	1.0
Pd	15.3±0.3	1–500	0.3
Ir	1.95±0.02	2–500	1.0
Rh	20.9±0.2	1–500	0.3

[a] Calibration equation $y = bx + a$, where y is the peak area in μV min^{-1} and x is the metal concentration in ng per 20 μl of sample. Seven points each calibrate with three replicates (RSD = 4%).

Acknowledgements

This research has been supported by the CICYT (Spanish Commission for Research and Development), Project No. QUI96-1025-C03-03.

References

[1] I.P. Alimarin, E.M. Basova, T.A. Bol'shova, V.M. Ivanov, J. Anal. Chem. 41 (1986) 1.
[2] J. Havel, A. Khramov, Scripta Fac. Sci. Nat. Univ. Masaryk. Brun. 27–28 (1997) 51.
[3] B. Wenclawiak, F. Bickmann, Bunseki Kagaka 33 (1984) E67.
[4] I.P. Alimarin, E.M. Basova, A.Y. Malykhin, T.A. Bol'shova, Talanta 37 (5) (1990) 485.
[5] B. Wenclawiak, A. Eicke, W.K. Sichtermann, A. Bennighoven, Fresenius Z. Anal. Chem. 329 (1987) 447.

[6] A.Y. Malykhin, T.A. Bol'shova, I.M. Ermolenko, I.B. Bobrovich, I.A. Nikishkin, L.A. Polyakova, J. Anal. Chem. 44 (1989) 724.
[7] J.M. Sánchez, V. Salvadó, J. Havel, J. Chromatogr. A 834 (1999) 329.
[8] B.A. Bidlingmeyer, Practical HPLC Methodology and Applications, John Wiley, New York, 1992.
[9] A.B. Benediktov, A.V. Belyaev, Koord. Khim. 10 (1984) 1516.