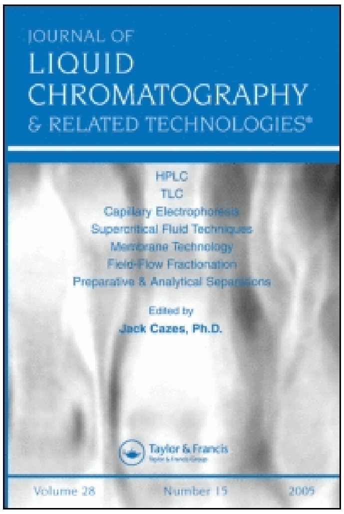

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Determination of Platinum and Rhodium in Pt-Rh Catalysts by TLC in SITU

Z. Šoljic[a]; S. Jurlina[a]
[a] Department of Analytical Chemistry, Faculty of Chemical Engeneering and Technology, University of Zagreb, Zagreb, Croatia

To cite this Article Šoljic, Z. and Jurlina, S.(1996) 'Determination of Platinum and Rhodium in Pt-Rh Catalysts by TLC in SITU', Journal of Liquid Chromatography & Related Technologies, 19: 5, 815 — 821
To link to this Article: DOI: 10.1080/10826079608005539
URL: http://dx.doi.org/10.1080/10826079608005539

J. LIQ. CHROM. & REL. TECHNOL., 19(5), 815–821 (1996)

DETERMINATION OF PLATINUM AND RHODIUM IN Pt-Rh CATALYSTS BY TLC IN SITU

Z. Šoljic, S. Jurlina

Department of Analytical Chemistry,
Faculty of Chemical Engeneering and Technology
University of Zagreb,
Marulicevtrg 20, 41000 Zagreb, Croatia

ABSTRACT

Favourable chromatographic conditions for separation of Pt and Rh were achieved on microcrystalline cellulose with solvent system methylisobutyl ketone - conc. HCl (40+60, v/v) and KI in ethanol as detection reagent; narow, compact and coloured bands on white background (R_F 0.44 for Rh and 0.76 for Pt) were obtained.

Convenient conditions for photometry in situ (maximum absorption at 480 nm for Rh and 510 nm for Pt; range of linearity from 0.06 μg/cm to about 1.5 μg/cm) were also established.

Worked out procedure was employed to analyze standard solutions and samples of catalysts (ingots). Results obtained have shown that the method is sufficienthly accurate and suitable for simultaneous quantitative determination of Pt and Rh.

INTRODUCTION

Platinum and rhodium alloys are applied in the industry of fertilizers as catalysts. Their manufacturers analyze various samples of catalysts (ingots, powder, filter mass and net). Gravimetric methods[1,2] are the most employed, but are time-consuming, complicated (comprise a whole range of operations) and costly (high quantities of samples, large number and volume of reagents).

Present investigation was aimed to study the convenience of TLC in situ for simultaneous determination of platinum and rhodium in the aforementioned samples of catalysts. Several authors studied the applicability of paper chromatography[3] and TLC on Al_2O_3 and silica gel layers[4] for separation and detection of the group of platinum metals. In this work we used microcrystalline cellulose.

MATERIALS AND METHODS

The experiments were carried out on TLC plates precoated with microcrystalline cellulose, (E. Merck), 20x20 cm, thickness of layer 0.1 mm.

Preparation of Standard Solutions

Standard solutions were prepared from H_2PtCl_6 and $RhCl_3x3H_2O$ (E. Merck) by dissolution of required amounts in HCl solution, *c*(HCl) =0.1 mol/L. The concentration of Pt and Rh in standard solutions were within the range 0.001 to 2 mg/mL.

Application of Standard and Sample Solution

Was performed with the CAMAG LINOMAT IV: 10 μL in band along 10 mm; 10 mm distance between bands; 4 bands of standards and 5 bands of samples were applied to the plate.

Development

Was carried out in CAMAG chromatographic chamber (saturated with developer for 30 minutes). Developer: methyl-isobutyl ketone - HCl conc. (40+60 v/v).

Visualisation

Was performed by spraying with 1% solution of KI in ethanol (sprayer with compressed air). Preparation of KI solution: dissolve 1.0 g of pure KI in a small volume of water and add ethanol to 100 mL. After spraying with KI solution, warm the plate in draying oven at 100 °C for 30 minutes.

A Camag TLC/HPTLC scanner (scanning rate: 3 mm/s, slit: 4/5, sensitivity: 50) was used for densitometry of Pt and Rh bands at 510 nm and 480 nm respectively.

Preparation of Sample Solution from Pt-Rh Ingot:

Weigh (using analytical balance) 0.20-0.25 g of the ground sample, place in a glass vessel and add 20-25 mL of aqua regia. Cover with the watch glass and warm on the hot plate (at 85-90°C). When dissolved, uncover and evaporate to almost dry. Add 1.2 mL of concentrated HCl (to cover the syrup precipitate) and evaporate again to almost dry. Add HCl, *c*=0.1 mol/L, to the precipitate to dissolve completely. Transfer the solution quantitatively into a 1000-mL volumetric flask, add the solution of HCl, *c*=0.1 mol/L and shake vigorously.

RESULTS AND DISCUSSION

Optimal conditions for separation of rhodium and platinum by TCL, as well as their direct and simultaneous determination on a thin-layer were established experimentally. Out of the several solvent systems studied, methyl-isobutyl ketone - HCl conc. (40+60 v/v) gave the most satisfactory results. That solvent system produced separated, narrow, compact Rh and Pt bands. The obtained R_F values for Rh and Pt were 0.44 and 0.76 respectively. Developing time for 10 cm length was around 3.5 hours.

Studied were several reagents for detection of Rh and Pt (PAN, NaDDTC, cinchonine, KI). Ethanol solution of KI, showed superiority for having produced intensely coloured bands against white background: dark brown for Rh and pink-brown for Pt. That selective reagent allowed uniform and fine spraying when the sprayer was connected to compressed air.

The most convenient conditions for photometry on TLC/HPTLC Scanner were determined experimentally. Detected were wavelengths of maximum

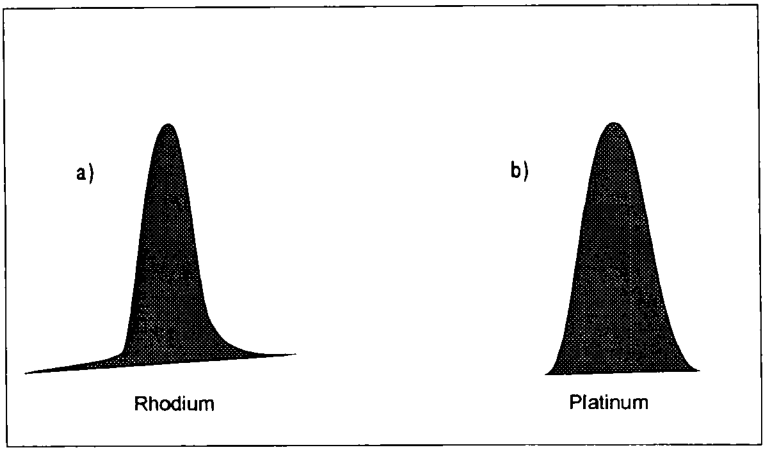

Figure 1. Photometric curves of rhodium and platinum bands a) γ (Rh)=0.469 μg/cm, R_F=0.44; b) γ (Pt)=0.52 μg/cm, R_F=0.76; thin layer: microcrystalline cellulose; developer: methyl-isobutyl ketone - HCl conc. (40+60, v/v); reagent for detection: 1% solution of KI in ethanol.

absorption: λ = 480 nm for Rh and λ= 510 nm for Pt. The lowest recordable limit concentrations of the solutions were about 0.006 mg/mL (i. e. 0.06 μg/cm with the application of 10 μL) for both Rh and Pt. Established range of solution concentrations, most convenient for measuring, was from 0.006 mg/mL (0.06 μg/cm) to approx. 0.14 mg/mL (1.4 μg/cm) for Rh and up to approx. 0.16 mg/mL (1.6 μg/cm) for Pt. That concentration range showed linearity between the areas under photometric curves and the quantity of studied ions in the band (correlation coefficient is 0.999). Photometric curves were almost symmetrical Gaussian curves (Figure 1).

The developed TLC in situ method gave sufficiently accurate and reproducible values, as compared with the known quantities of rhodium and platinum standards applied to the layer (Table 1).

The results obtained by this method for Rh and Pt in the samples of catalysts were well in agreement with those obtained by gravimetry (Table 2). Consequently, it is possible to employ the diveloped TLC in situ method for simultaneous quantitative determination of rhodium and platinum in Rh-Pt-catalysts, applied in the industry of fertilizers. The method is simple, cost-saving and rapid (unlike gravimetry). Its particular advantage is in that it allows simultaneous separation and determination of rhodium and platinum

Table 1

Comparison of Rh and Pt Values Obtained by TLC In Situ and Amounts Applied to Thin Layer

Rh/(μg)		Pt (μg)	
Applied	**Determined**	**Applied**	**Determined**
0.088	0.8600	0.0975	0.0970
	0.0865		0.0968
	0.0870		0.0980
	0.0876		0.0960
	0.0885		0.0969
0.469	0.4650	0.520	0.5180
	0.4630		0.5185
	0.4710		0.05176
	0.4670		0.5230
	9.4730		0.5180

which, in turn, simplifies and shortens the procedure itself and duration of analysis. The analysis can be performed on one sample solution if the mass fraction of one element in the sample is below 65% and of the other over 5%. In such instances it is necessary to weigh 0.20-0.25 g of the sample, dissolve it and make with HCl solution, c=0.1 mol/L, to 1000.0 mL. Rh and Pt concentrations in the obtained solution are within the range of linearity. The solution should then be applied to chromatoplate in 5 bands and parallely 4-5 bands of standards; results of determination are mean values of parallel determinations for both Rh and Pt. If the sample composition is other than the stated (i. e. if the ratio of these elements exceeds 13:1), two sample solutions should be prepared. Since the Rh and Pt content limits being known for each catalyst sample during the production, sample weight and solution volume can be calculated. In that way the concentration of the element contained in the sample in a lower quantity is brought to the linearity limits (solution 1). The aliquot of this solution has then to be diluted to a specified volume, in which the concentration of the element having higher mass fraction, is now brought to the linearity range of the method (solution 2). Three bands of solution 1 and three bands of solution 2 are applied to chromatoplate and chromatography and densitometry carried out. Mean values of three parallel determinations for every element represent results of the determination.

Table 2

Comparison of Quantitative Determination of Rh and Pt in PT and Rh Alloys (Ingots) by TLC In Situ and by Gravimetry

	TLC In Situ		**Gravimetry**	
Sample (Ingot)	**Rh/(%)**	**Pt/(%)**	**Rh/(%)**	**Pt/(%)**
1	13.89	85.56	13.80	85.34
2	14.01	85.60	14.30	84.99
3	13.98	85.87	13.70	85.50

This TLC in situ method gives satisfactory results, the standards and samples being chromatographied and photometered under equal conditions and simultaneously, which annuls the errors. It is important that the standards be very pure chemicals and that the analysis be carried out with care and accuracy. Dissolution of samples represents major difficulties. Using aqua regia for dissolution is very time-consuming (takes four and more hours). If rhodium content in a sample is high, the sample is then slightly soluble in agua regia. Therefore, an indissoluble part has to be melted with $NaHSO_4$ or $Na_2S_2O_7$ and the melt dissolved in HCl.

Compared to gravimetry, this TLC method requires analytical samples of significantly smaller weight, contained in the big volume of the solution. Therefore small amounts of silicon, which may occur in some samples of catalysts (as filter mass), will not produce noticeable errors. One of the advantages of TLC method for Rh and Pt determination is in that it does not require removal of the impurities in the catalyst samples (Cr, Ni, Fe, Mn and Pd) from the sample solution, as they do not interfere with determination procedure.

REFERENCES

1. F. Bimish, **Analitičeskaja Himija Blogorodnih Metallov**, Himija, Moscow, 1969.

2. I. F. Barbshnikova, **Probootbiranie I Analiz Blogorodnih Metallov**, Himija, Moscow, 1968.

3. J. Michal, **Inorganic Chromatographic Analysis**, Van Nostrand Reiholds, London, 1973.

4. U. A. Th. Brinkman, G. J. De Vries, J. Chromatogr. (Chromatogr. Review), **85**, 234-459 (1973).

Received June 12, 1995
Accepted June 23, 1995
Manuscript 3907