

Recycling and Reuse Technology Transfer Center

Recycling and Reuse Technology Transfer Center



<http://www.rrttc.uni.ed>

Determination of Platinum Metals by Ion-Pair Chromatography

Publication: 1994 – 019

Cindy X. Shen, Duane E. Bartak, Ching S. Woo

Presented at the Ninth Annual Ames/Iowa Joint
Meeting of the American Chemical Society,
April 16, 1994

**DETERMINATION OF PLATINUM METALS
BY ION-PAIR CHROMATOGRAPHY**

Cindy X. Shen, Duane E. Bartak, Ching S. Woo
University of Northern Iowa

ABSTRACT.

Ion-pair chromatography has become recognized as an effective technique for the separation of anionic species. One approach of special interest is the application of reverse-phase columns which are treated with a cationic modifier (ion-pair reagent). This modified phase on the column together with the ion-pair reagent in the mobile phase are used to separate the chloro- or bromo-anionic metal complexes.

In this work, we report the use of octadecyl-bonded silica and macroporous polymer columns with an acetonitrile-water mixture containing an ion-pair reagent, tetrabutylammonium fluoroborate, to separate rhodium, palladium, and platinum metal complexes. The chloro-anionic complexes were detected at 255 and 310 nm, and quantitative results were obtained by both the calibration and standard addition methods. The techniques were successfully applied to the analysis of platinum group metals in samples of spent automotive catalysts.

INTRODUCTION.

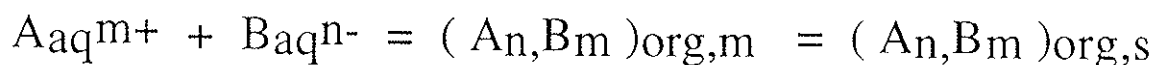
This research is the result of an environmental project, which is concerned with the recovery of platinum group metals (platinum , palladium and rhodium) from automobile catalytic converters . The objective of the project is to develop commercially viable methodology to reuse and recycle the precious metals which have been required to be used in catalytic converters of automobiles by Federal legislation since 1975 (Pd and Pt) and 1983 (Pd, Pt, and Rh) in the U. S. Platinum and palladium catalyze the conversion of carbon monoxide (CO) to carbon dioxide (CO₂). Rhodium plays an important role in catalyzing the reduction of NO_x to N₂. NO_x and CO are two major air pollutants, which result from internal combustion engines. Because of the catalytic applications of these three metals to automobile converters, the automobile industry of the U. S. is the major consumer of the metals. Currently approximately 10% of these precious metals are recycled and reused. Technologies which are environmentally friendly and economically viable need to be developed.

As a part of the project , it was necessary to develop a new analytical method for the rapid separation and simultaneous determination of the mixture of chloride complexes of platinum group metals by high-pressure liquid chromatography (HPLC).

Platinum group metals can be dissolved in water in several complex forms including chloride, bromide, and thiocyanate; however, the chloride complex form is the most cost effective. Hence, this complex was used as a starting material in the recycling strategy. There are methods to analyze the three metals; however, some are limited in scope and time consuming (e.g., solvent extraction followed by atomic absorption spectroscopic (AAS) analysis).

Ion chromatography has become the dominant analytical technique for determining the inorganic anion since 1975; however, most of the applications were limited to simple anions, such as Cl^- , F^- , and NO_3^- . The very strong sorption of highly charged chloride complexes of the platinum group metal anions on the conventional anion-exchange resins makes it difficult to elute and separate the metals.

A new method to determine platinum, palladium, and rhodium by ion-pair, reverse-phase HPLC will be presented in this report. Tetrabutylammonium fluoroborate (TBABF) will be used as an ion-pair reagent in the mobile phase, which consists of a mixture of acetonitrile and water, and the C18 column as the stationary phase. The principle of the contact ion-pair HPLC is based on the equation:



A^{m+} is the counter ion (e.g., tetrabutylammonium ion) and B^{n-} is sample ion ($RhCl_6^{-3}$, $PdCl_4^{-2}$, and $PtCl_6^{-2}$) in in this work. The subscripts, s and m, refer to the stationary and mobile phase. The ion-pairs form as a result of the presence of ion-pair reagent (e.g., tetrabutylammonium ion) to the aqueous phase. The resultant ion-pair complex has a low net electrical charge or polarity and is thus poorly hydrated and partitions readily to organic phase. The retention of the ion-pair is dependent on several parameters including: (1) nature and concentration of pairing ion analyte, (2) mobile phase, (3) stationary phase, (4) temperature, (5) pH, (6) ionic strength and (7) counter-ion size (i.e., hydrophobicity) and concentration. It has been demonstrated that small changes in these parameters can affect separation and thus by optimizing these parameters, very rapid and highly selective separation can result. It is usually more convenient and more efficient to vary the concentration and the size of the counter-ion (e.g., tetraethylammonium ion vs. tetrabutylammonium ion) or the ratio of organic/inorganic solvents in the mobile phase. The advantage of using tetraalkylammonium ions is that these ions are aprotic and may therefore be used at all pH values. Variation of the size of the tetraalkylammonium ion will affect the partition co-efficient of the contact-ion pair and thus attain the desired selectivity.

EXPERIMENTAL

1 . Apparatus

Liquid chromatographic analysis was performed with a Spectra - Physics HPLC system which has a ternary reservoirs , A , B , and C . For our experiments , A reservoir was with water , B was with acetonitrile , and C was with a certain concentration of TBABF in the solvent of $\text{H}_2\text{O} / \text{CH}_3\text{CN}$. The composition of mobile phase will depend on the ratio of A / B / C . The system were equipped with a Val - U - Pak HP C - 18 column , 25 cm x 4.6 mm i.d. , a Spectroflow 757 variable - wavelength UV - visible detector , and a Spectra - Physics integrator .

2 . Preparation of TBABF solution (for reservoir C) .

The solution in reservoir C was prepared in the two way :

C 1 : weighted . 0025 mol . TBABF and dissolved it in 1000 ml solvent of % 70 of water and % 30 of acetonitrile . The concentration of TBABF was . 0025 M .

C 2 : weighted . 0625 mol . TBABF , .03125 mol . ammonium floroborate , and .0125 mol . phasphate and dissolved them in 1000 ml solvent of % 65 of water and % 35 of acetonitrile . The conc. of TBABF was .0625 M .

The solutions were then filtered through a . 5 - mm membrane filter .

3 . Preparation of standards .

Standard I :

standard I were prepared as followed : 2000 ppm solutions of rh , pd , and pt were prepared separately by dissolving commercial reagents of Na_3RhCl_6 , Na_2PdCl_4 , and K_3PtCl_6 with .1 N HCl / .2 NaCl . And then prepared the standards by using different aliquots , which gave standards with the concentrations of rh , 100 , 200 , 300 and 400 ppm , pd , 100 , 200 , 300 and 400 ppm , pt , 200 , 400 , 600 , and 800 ppm .

Standard II :

5 ml extract from catalytic converter was added to each of 5 25 - ml volumetric flasks . Aliquots (0 , 1 , 2 , 3 and 4 ml of 2000 ppm pd solution) and aliquots (0 , 3 , 6 , 9 and 12 ml of 1000 ppm pt solution) were transferred to the flasks containing the extract . The contents of the flasks were diluted to volume with .1 HCl / .2 NaCl . This gave standards containing 0 , 80 , 160 , 240 and 360 ppm of pd , and 0 , 120 , 240 , 360 and 480 ppm of pt , respectively .

4. Analysis of standards .

a . A 20 - ml aliquot of each standard I , standard II was analyzed by HPLC . The chromatographic conditions were as follows : general elution ; mobile phase = % 100 C 2 ; pH = 7.2 ; flow rate = 1 ml / min ; detector wavelength = 255 nm ; attenuation of integrator = 256 .

b . . A mixture of .004 M of rh / pd / pt was analyzed by HPLC . The chromatographic conditions were as follow : gradient elution ;

mobile phase :

Time (min) \ % solution	A	B	C
0	0	10	90
5	0	15	85

5 . Analysis of spent automotive catalysts .

Samples were analyzed by HPLC . The chromatographic conditions was the same as the conditions used for analyzing standard I and standard II .

6 . Dissolution of spent automotive catalysts .

Added 5 g of each of the finely ground automobile converter material and sodium peroxide to a 100 - ml metallurgical alumina crucible . placed the crucible in a muffle furnace at T = 450 °C 15 min . Then , the cooled crucible was placed in a 300 - ml beaker . Added 50 ml of 1 : 1 HCl to the beaker and heated the beaker to make sure that all the metal oxides were dissolved . Filtered the content under suction . The filtrate was quantitatively transferred to a 250 - ml volumetric flask and adjusted volume upto the mark with water .

Case report 11-2014

* RESULTS AND DISCUSSION.

Figure 1 illustrates the separation of mixture of chloride complexes of Rh, Pd, and Pt by HPLC using gradient elution. RT (retention time) of Rh = 2.45 min., Pd = 4.62 min., Pt = 6.20 min.

Figure 2. Calibration curve of rhodium using HPLC, Method I.

Figure 3. Calibration curve of platinum by HPLC, Method I.

Figure 4. Calibration curve of palladium by HPLC, Method I.

Figure 5. Calibration curve of palladium by HPLC, Method II.

Figure 6. Calibration curve of platinum by HPLC, Method II .

Figure 7 illustrates a series of chromatograms obtained using Method II . RT of Pd=3. 94 min., Pt = 12 .88 min.

Figure 8 shows the chromatograms obtained with extracts # 2 ,# 3 , and # 6 from spent catalysis material. The amounts of Pt/Pd found in the converters were determined Method I and Method II.

Figure 9 shows a series of chromatograms using Method I for calibration.

Table I . Determination of Platinum and Palladium in Spent Converter Material by Method I.

sample #	Palladium (mg/kg of catalyst)	Platinum
2	-	1233
3	-	1819
6	694	1250

The analysis of palladium and platinum in sample #3 by HPLC with Method II was also carried out. The results showed that there was 1736 mg of platinum /kg catalyst and 278 mg of palladium/kg of catalyst. Comparisons of the result from Method I with Method II indicate slightly higher levels using Method I.

CONCLUSIONS.

A simple and accurate technique for determination of low levels of palladium and platinum has been developed. The results were reproducible and reliable. The technique has been applied to the separation and analysis of palladium and platinum from spent catalysis material. The results show that the contact-ion pair HPLC method is useful for quantitation of palladium and platinum for our project as well as for general analysis .

Fig. 8 Chromatograms of extracts of # 2 , # 3 and # 6 catalytic converters .

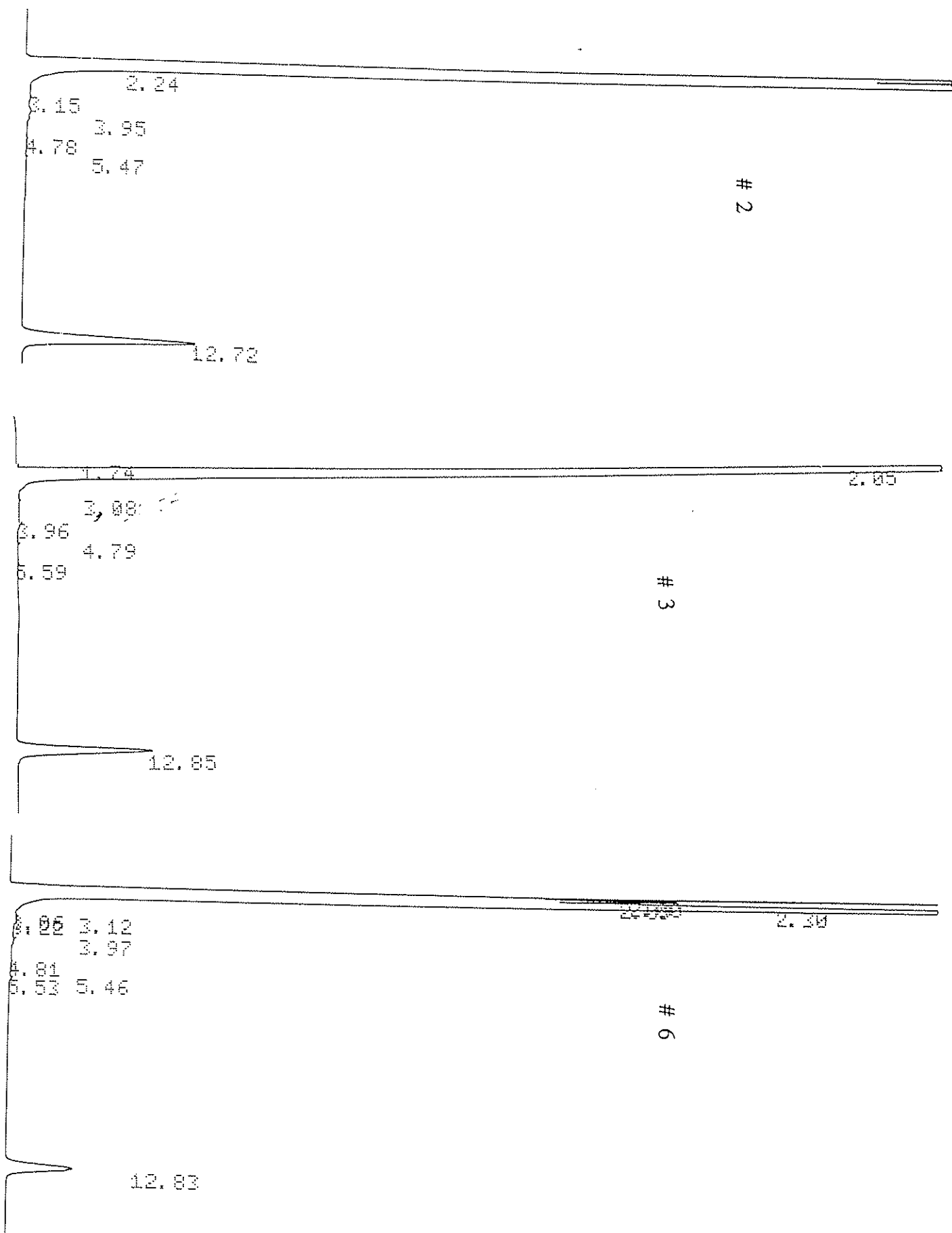


Fig . 9 A series chromatograms of standard I .

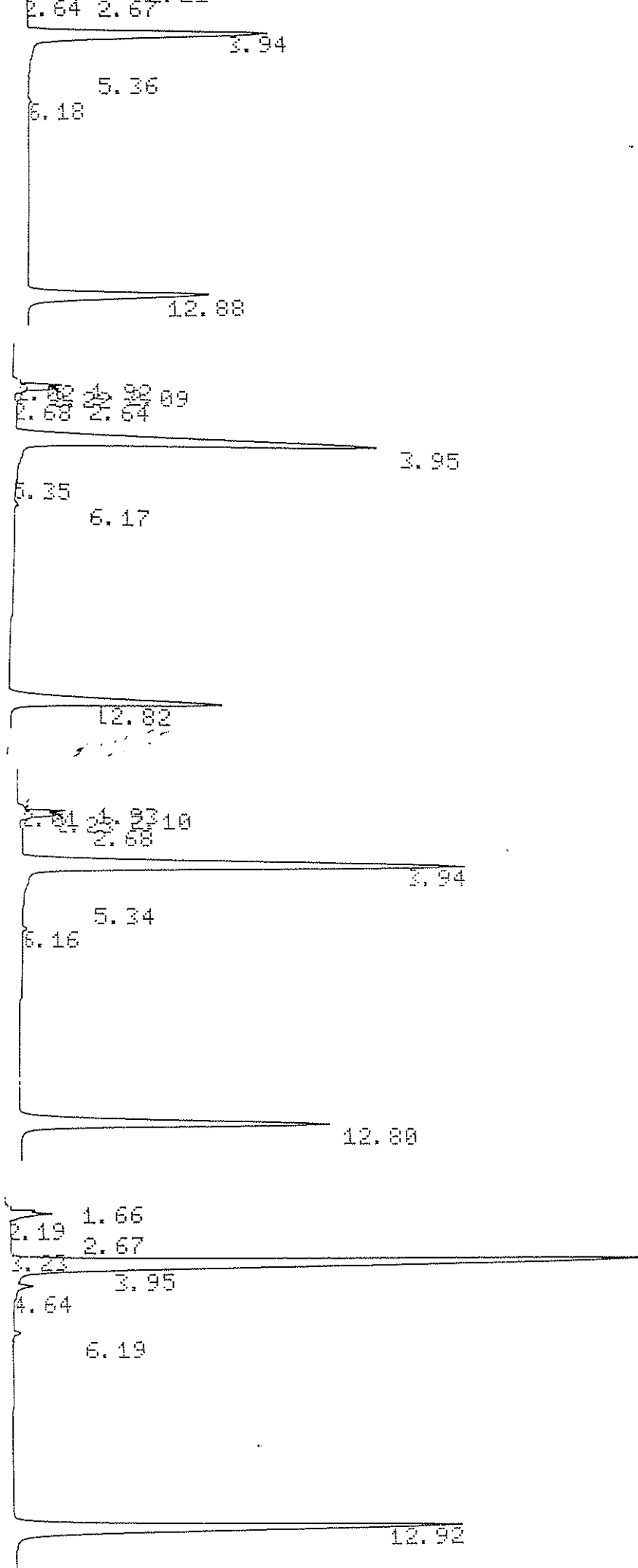


Fig. 8 Chromatograms of extracts of # 2, # 3 and # 6 catalytic converters

