Stripping Platinum Metals from Catalytic Converter Units by Use of Promoted Gas Phase Chlorine Attack

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STRIPPING PLATINUM METALS FROM CATALYTIC CONVERTER UNITS BY USE OF PROMOTED GAS PHASE CHLORINE ATTACK

BY

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B.S., Florida Technological University, 1974

RESEARCH REPORT

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ABSTRACT

STRIPPING PLATINUM METALS FROM CATALYTIC CONVERTER UNITS BY USE OF PROMOTED GAS PHASE CHLORINE ATTACK

A gas-phase system to oxidize and remove the platinum and palladium from automotive catalytic converter units was studied. The effects of varying reaction temperature, time and reactant gas concentration upon yields were monitored using a colorimetric procedure based on the reagent p-nitroso-N,N-dimethyl amiline. Chlorine plus carbon monoxide at 700°-900°C displayed the most promise for commercial application.
ACKNOWLEDGEMENT

The professional direction and assistance of Dr. Chris Clausen III have been invaluable and memorable in so many ways. Professors Hertel, Idoux, Madsen and Mattson all furnished special advice in this work and on many other topics over the past decade of my schooling at UCF. My parents' financial and social aid has also been greatly appreciated.
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INTRODUCTION

I. The Catalytic Converter and Its Metallic Content

The efforts described herein are aimed at completing one portion of a picture, that picture being the technology for converting unacceptable and toxic automotive exhaust gases to environmentally compatible compounds before they leave the vehicle.

The symptoms of unchecked emissions became of sufficient public and governmental concern to bring about enactment of much legislation on the topic. The Federal Clean Air Act of 1970 called for a 90% reduction by 1975 in the average 1970-71 levels of carbon monoxide (CO), unburned hydrocarbons ("HC") and nitrogen oxides ("NOx") exiting engines.

Various innovations to increase the completeness of engine combustion, such as "E.G.R." systems (exhaust gas recirculation) and the PCV device (positive crankcase ventilation of crankcase fumes back into the
combustion chambers) proved insufficient to meet the new law mandates. As a result, the automobile manufacturers developed a secondary reaction system to complete the job of oxidizing CO to CO₂, and "HC" to CO₂ plus H₂O, as well as that of reducing NOx to N₂ gas. The primary component in this secondary system is the "catalytic converter," which consists of a set of one or more monolithic ceramic-based blocks with a honeycomb-like interior, often encased in stainless steel; the blocks bear trace amounts of metals, usually in their elemental state or in oxide form.

Exhaust gas flow is maintained through the blocks by a difference between engine manifold and outside air pressures. Most blocks are maintained at 300°-400° F. with conversions of the exhaust gases taking place on the many surfaces throughout the converter block's interiors, prior to entry of the gases into the system's muffler.

The platinum-group metals -- ruthenium, rhodium, palladium (Pd), osmium, iridium, and platinum (Pt)
(the group will hereafter be referred to as the PGM, with special emphasis on Pd and Pt) have been chosen above many other possible and patented candidates for use in the catalytic converter units manufactured in the U. S., Japan and most European nations.

Numerous studies throughout the early 1970's showed many of the base metals considered as useful agents for catalyzing exhaust gas conversions to be plagued with difficulties such as "poisoning," the irreversible chemical reactions of the metals to inactive surfaces, and fast "aging," short active life of catalyst due to reformation to inactive surfaces. Typical candidates were supported combinations of the first row transition metals including the elements vanadium to copper (1). Catalyst monoliths containing levels of 0.1 to 0.5% total weight of platinum and palladium have been used for cars and trucks built in the U. S. since 1975, with rhodium and ruthenium receiving consideration for future high performance units. The catalytic converters are designed to operate efficiently for 50,000 road miles.
As the units are designed to offer the maximum active surface area to the total incoming exhaust flow with minimal resistance to the flow, pretreatment of the flow to remove solid particles or agents which would poison the catalyst is impractical. Deactivation of the PGM catalyst systems can be blamed on several factors, including: 1. The reduction of organometallics such as those from leaded fuels upon surfaces of the honeycomb interior and thereby blocking access to active PGM atoms and crystals; 2. Unburned carbonaceous and metallic particles likewise settling over "active" sites; 3. A tendency for small Pt crystallites to gradually reform to larger structures, thus lowering the ratio of available surface area to mass; 4. Loss of PGM from the catalytic converter via oxidation and volatilization as organometallics.

In 1977, the demand for platinum for use in converter ovals rose by 5%, to a level of 0.74 million troy ounces, this being 45% of the total U. S. Pt consumption (2). Since the U. S. A. has no significant deposits of the PGM, it must import amounts sufficient
to fill the gap between a rising demand and the platinum metals currently recycled domestically. Important exporters of PGM such as Canada and South Africa face potential political upheavals which might halt their production, and the U.S.S.R.'s ample reserves of those metals can be and often are cut off to the U.S. If automotive production and the mandates for clear air are to continue, used converters will have to be recycled; the rising prices for the PGM should provide the incentive.

Few discussions specifically describing recovery of the PGM from automotive catalytic converter units were reported in the media or chemical literature through 1977, and the author chose to pursue investigation of a recovery system used on other PGM-bearing scrap materials.

II. Chemical Attack of the Platinum Group Metals

This report examines removal of platinum and palladium from catalytic converter supports selected for use in the U.S., with consideration of choosing
optimum conditions for metal removal while using industrially feasible equipment and reagents. Specifically, the study focused on a gas-phase chemical attack of the supported Pt and Pd, and their separation from the support matrix.

Few materials possess a potential for attack upon Pt and Pd, via gas -- or liquid -- phase reactions. The earliest and still most commonly-used reagent for chemical attack on the PGM is via a hot "aqua regia" acids solution. Such a solution is most effective against Pd and Pt. The other PGM are highly resistant, except in the finely-divided metallic "blacks" form, or alloyed with other, "baser" metals. Aqua regia usage was retained in this study for comparison of its proven effectiveness to the results from attack of various oxidizing gases upon the catalysts.

Of prime and practical interest is removal of the PGM catalysts without destruction or dissolution of their silico-alumina ceramic supports. Avoiding such dissolution would be a savings of reagents and energy and might allow reuse of the supports in some other
application. Removal of desired PGM species as volatile, distillable compounds by gas-phase sweeping of the supports can also be adapted to a labor-saving continuous-type refining system if the necessary conditions for a high degree of separation are economically and technically feasible. For example, dry gases, both reactants and product-containing flows, might involve less storage space than a combination of various reactant, rinse and product-bearing acid solutions, and would probably involve less costly pollution control equipment and processes than a liquid system.

III. "Chemistry of Platinum and Palladium"

Many common industrial acids, oxidizers and alkalies, such as HCl, H₂SO₄, HNO₃, NaOH, and Cl₂, often in combination with lesser amounts of agents such as CO, NO, H₂S and ethylene, have been considered for practical chemical attack of the PGM. Conversion to the chlorides and their "adducts" with other non-metallic species usually show the most promise, as most of these combinations are water-soluble and
more kinetically stable; many PGM nitrates, sulfates or other non-halides are unstable and ill-defined at STP.

An important and typical reaction is:

\[ \text{Pt}(s) + 2 \text{Cl}_2(g) \rightarrow \text{PtCl}_4(\text{solid or gas}) \text{ (or as } \text{PtCl}_6^2(aq) \text{) in presence of NOCl, HCl, etc.} \]

Platinum tetrachloride easily forms the hexachloride aqueous media and moderate solubility in several polar solvents, such as ethyl acetate and diethylether. In gas-phase attack, the volatility of \( \text{PtCl}_4 \) helps to rapidly expose new surface area for chemical attack. Both the tetrachloride and platinum's dichloride have significant volatilities above 700°C (3). Pt combines in all four of its observed oxidation states with chlorine, with \( \text{PtCl} \) and \( \text{PtCl}_3 \) existing over defined ranges well above room temperature (4). Discussions of platinum chlorides preparation often suggest the formation of \( \text{PtCl}_4 \) at 270°C-350°C by direct gas-phase union of the elements, and claim that the reaction proceeds through \( \text{PtCl}_3 \) to a water-insoluble \( \text{PtCl}_2 \) as heating elevates temp-
erature past $450^\circ$ (5,6). Other research dealing with mixtures of platinum chlorides and sodium or potassium chloride has suggested the existence of volatile $\text{PtCl}_4$ and of $\text{PtCl}_2$ at temperatures up to $1400^\circ$ C. (7). The predominance of a volatile $\text{PtCl}_2$ between $455^\circ$ and $650^\circ$ C., with equilibrium shifted to only $\text{PtCl}_4$ above $700^\circ$ C. is reported (8). Such research has suggested the utility and feasibility of high temperature distillations of platinum chlorides and other related PGM species for analysis and for recovery.

Literature data concerning the volatility of palladium dichloride and transition points for sublimation are diverse and contradictory. $\text{PdCl}_2$ has been called relatively "volatile" up to $700^\circ$ C. (3), while other researchers have claimed $300^\circ$-$350^\circ$ C. to be the optimum sublimation range (9). These same Russian researchers reported that $\text{PtCl}_4$ was only 51-85% volatilized over the same range (9). A melting point of $678^\circ$-$680^\circ$ C. (under a pressure of two atmospheres in chlorine gas) has been determined for $\text{PdCl}_2$ (10).
When chlorine is used in combination with other gases to attack Pt and Pd, volatile species other than the binary chlorides can be obtained at elevated temperature. CO and NO are the most studied co-reactants in such systems. Usage of other nitrogen oxides, phosphorous pentachloride, and aluminum trichloride are also reported in such efforts (11, 12).

The periodic table's "family" of nickel, palladium, and platinum all form established carbonyl complexes or carbonyl halides. Nickel carbonyl, Ni(CO)$_4$, is of economic importance in Ni purification metallurgy; a carbonyl halide complex for nickel is not reported. However, the stability of such complexes shows increased strength for palladium, and those with platinum are often stable at room temperature (13). Such complexes at 25°C and 1 atmosphere have been individually characterized (14, 15, 16, 17).

Platinum will react with phosgene (COCl$_2$) and its constituents (CO, Cl$_2$) at temperatures above 200°C to yield at least four distinct compounds stable at
room temperature. European journals detailed preparations of these as early as 1868-70 by reaction of $\text{Cl}_2 + \text{CO}$ at 240°-250° C. with Pt sponge and with PtCl$_2$ (18). Separation of such a reaction's products yielded Pt(CO)Cl$_2$, Pt(CO)$_2$Cl$_2$ and Pt(CO)$_3$Cl$_4$ (19). A related species reported in 1891 was initially thought to be \"Pt(CO)$_2$Cl$_6\" (20); however, later investigation revealed it to be a complex of COCl$_2$ with PtCl$_2$, or Pt(COCl$_2$)$_2$Cl$_2$ (21). A recent edition of the C.R.C. Handbook listed \"Pt(COCl$_2$)Cl$_2\" , stating that its decomposition precedes a melting point (22).

The compound Pt(CO)Cl$_2$ exists as a chloride-bridged dimer in the solid and vapor states (23), and is a stable orange-red solid at 25° C. It is readily soluble without decomposition in HCl and cold water, reportedly decomposing above 300° C. (19).

Further introduction of CO into the Pt (IV) complex under high pressure and temperature creates at least two more species -- Pt(CO)$_2$Cl$_2$ and Pt$_2$(CO)$_3$Cl$_4$ (24). They have lower decomposition temperatures
and high liabilities than Pt(CO)Cl₂; Pt(CO)₂Cl₂ has a sufficiently high solubility in CCl₄ relative to Pt(CO)Cl₂ and Pt₂(CO)₃Cl₄ to allow its complete separation by solvent extraction (24). Related species stable above 400°C. have not been reported.

Palladium complexes from direct union of the metal or PdCl₂ with Cl₂ and CO appear to be less stable than platinum counterparts. One review reports the existence of Pd(CO)Cl₂, Pd(CO)₂Cl₂ and Pd(COCl) (15). The later species decomposes at 250°C., with the others being unstable above 60°C. (25). No such complexes are believed to exist above 250°C. (15).

Discussions of the pi-bonding ability of CO often cite corresponding properties of the NO molecule. However, rather few studies of NO usage in the preparation of gas-phase or solid complexes with platinum metal chlorides have been reported. Perhaps higher costs of reagents, the great corrosion of NO towards handling equipment and the added toxicity are reasons for this lack of experimental efforts. Mellor's Treatise examined some of the scattered research on
such complexes prior to W.W.II. Of interest is the presentation of a model system for the production of nitrosyl chloride:

1) \( \text{NO} + 2 \text{Cl}_2 \rightarrow \text{NOCl}_2 \)
2) \( \text{NOCl}_2 + \text{NO} \rightarrow 2 \text{NOCl} \)

Kinetics data were cited in support (26).

Nitrosyl chloride (NOCl) has been used in the chemical attack and refining of the precious metals for centuries; it is considered to be the most active component in aqua regia mixtures, as it accomplishes what pure Cl\(_2\) often cannot. The widely accepted reaction leading to its generation is thought to be:

\[
\text{HNO}_3(e) + 3 \text{HCl}(e) \rightarrow \text{NOCl}(g) + \text{Cl}_2(g) + 2 \text{H}_2\text{O}(e)
\]

RT or higher

(the high solubilities of the gases somewhat decrease their release from the solution). Volume ratios of 3 to 5 parts HCl to 1 part HNO\(_3\) are utilized, with 5% to 20% water added to moderate the action. Heating to 70\(^\circ\)-110\(^\circ\) C. greatly increases emission of the active gases. NO\(_2\), or nitrogen dioxide (formed upon contact of air with NO), appears to aid the kinetics
of NOCl attack upon precious metals, yet NO₂ is unable to render the corrosion of gold or the PGM on its own (27).

References to NOCl in refining and assaying are often indirect, such as the frequent and necessary admonition that oxidations with aqua regia be followed by an "almost to dryness" evaporation/boiling of the solution. Depletion of nitrosyl chloride from such solutions is further aided by the addition of area, \((\text{NH}_2)_2\text{CO}\), or related compounds during heating.

Attempts to prepare a stable salt of Pt (IV) with NOCl have been described (28). Standard handbooks of inorganic compounds do not list any complexes of NOCl with Pt or Pd as being stable under conditions of 25°C and 1 atmosphere's pressure. A "wet" method published in the 1840's relied on dissolution of chloroplatinic acid, \(\text{H}_2\text{PtCl}_6\), in vacuum-filtered, washed with concentrated \(\text{H}_2\text{SO}_4\), then dried at 100°C (29). The product was believed to be tetrachlorodi(nitroglychloride) platinum, \(\text{Pt(NOCl)}_2\text{Cl}_4\) (28).
Another approach was based upon the introduction of distilled NOCl into sponge platinum of 100° C. (30).

A preparation of Pd(NOCl)₂ (originally named "palladous dinitrosyl chloride") has been reported; this di(nitrosylchloride) palladium (II) complex was unstable with respect to water, and any related forms were considered likewise unstable (31). A complex manufactured by flowing a mixture of NO and methanol vapor over anhydrous PdCl₂ at 50° C. has been cited, though with no suggestion as to the product's structure (32).

IV. "Proposed Systems for Attack of the PGM on Catalysts"

American patents have included several systems proposing chemical attack via gas-phase upon Pd and Pt impregnated catalyst, relative to the catalyst/support materials used in the petroleum industry for "reforming" of hydrocarbon chains into gasoline, etc.

One 1962 patent described its proposed system as "beneficial for cases where the ore (or scrap) containing a metal to be recovered is below the grade
required for economic recovery by methods heretofore known" (33,34). The patent's process involved a mixture of aqua regia heated and the generated NOCl and Cl₂ being distilled into a separate barrel-like chamber, with a trap in between for drying. The chamber could be agitated, and would allow a continuous flow of ore, chunks of catalyst, etc. for maximum contact of gases with exposed precious metals. Sublimed products/complexes would be recovered from a liquid trap, with a portion of the effluent gases recycled. It was specified that all material be crushed to 20 mesh or finer particle size prior to entry. A temperature range of 100⁰ to 1600⁰ F (38⁰-870⁰ C.) was said to volatilize only the desired PGM and gold salts, and convert iron to an insoluble, non-volatile oxide (33).

The continuous, rather than batch-type, nature of the process is noteworthy; in practice, precious metals refiners must often handle scrap batch-wise for owner settlement purposes, but a "recycler" of Pt-bearing
oval units would likely hold clear title to the entire lot and find attractive the operations and capital savings of a continuous process.

Other patented systems appeared in 1962, aimed at the removal of PGM from used or poisoned heterogeneous catalysts and related materials.

Two researchers at Universal Oil Products proposed the stripping (by sublimation of salts) of the PGM from inert supports by use of a NOx + AlCl3 vapor stream through the materials at 370°-600° C. (11). The process was batch-wise, as the PGM-bearing catalysts would be contained in a tube reactor of quartz, vycor or other non-porous refractory materials. A proposed loading scheme involved the PGM-bearing catalyst being "sandwiched" in a plug-flow: first, to meet in flow of gas streams, a "plug" of powdered AlCl3, followed by additional AlCl3 or alumina in a small "pills." Next came a section of glass wool, then the catalyst to be stripped, with a final glass wool plus. Hinged tube furnaces provided an elevated temperature (300° to 500° C.).
This 1962 patent also presented a brief review of previous approaches to gas-phase attack of PGM upon "spent" catalysts, claiming that the previous systems were unable to remove more than 70 to 95% of PGM content, compared to the patented system, using AlCl₃. A number of parallel treatments of a Pt-bearing catalyst (0.37% by weight) were presented, involving usage of binary or ternary mixes of N₂ plus Cl₂, CO, H₂S, etc.

One successful experiment was cited, where the Pt content was reduced from 3700 ppm to 5 ppm using a two-step system:

The first step involved passing air, N₂ and Cl₂ through the sample for 5 minutes at 500°C; the second step involved addition of powdered AlCl₃ to the PGM-bearing catalyst, followed by a flow of N₂ at 500°C for a time period sufficient to result in the catalyst changing color from gray/brown to cream-white (35).

A comparison experiment of the system's effectiveness using Cl₂ or AlCl₃, plus CO, was not discussed or proposed. The possibility of using pressures above one atmosphere to reduce necessary
reactant contact time or optimum temperature was noted, but not demonstrated, in the patent disclosure.

Midway through work on the present project, an abstract appeared in the Chemical Abstracts describing a proposed method for stripping Pd and Pt content from used automotive catalytic converter blocks via a gas-phase process (36). The abstract cited the patent of a two-step approach to removing PGM from used catalysts. The two-step process was as follows:

In Step A, a reactor holding the catalyst is maintained at 150°-250° C., and receives a gas flow containing 5% (by volume) or more of CO, COCl₂, and Cl₂, carried by an inert stream (N₂ or Ar) for 1 to 2 hours.

A more specific sequence was also presented, to treat a Pt and Pd-bearing sample:

Step A: 250° C., for 1 hour, with gas flow of 40% each of Cl₂ and CO, plus 20% COCl₂ (no specific volumes were given in the abstract).

Step B: 470° C., for 3 hours, with a gas flow of 10% CO, "in a specified reactor equipped with slit vanes to recover the metals" (36).
The study described in this research report has strived to further explore the usefulness of the Cl₂/CO and Cl₂/NO gas combinations in attacking different types of automotive catalytic converter units. The effects of gas-phase concentration, contact times, and temperatures on metal recovery yields have received the major attention. Possible extensions not experimentally explored but which appear potentially fruitful are suggested as well.
EXPERIMENTAL

I. Catalyst Samples for Study

A. Sample Size/Particle Size

Catalytic converter units from Ford Motor Company and Chrysler Corporation were studied. Representative portions of supported catalyst (hereafter referred to as "S/C") were collected from three or more geographically isolated areas of a sampled converter oval by means of hacksaw and plastic-headed mallet; 50 to 100 gram portions served to diminish any non-uniform PGM concentration's effects upon analysis. The converter units all contained two oval blocks; in each case, S/C samples were from the "forward" member of the pair -- the oval block closest to the engine.

The three to six gram samples of S/C for experimental study consisted of small "chunks" and granules from the larger weights of S/C previously described, with 90% or more by weight being
particle sizes 4 to 40 mesh (U. S. standard sieve sizes). Larger chunks were difficult to load and unload from the gas-phase treatment apparatus, and the lower surface to area ratio for finer sizes of particles was felt to lessen the desired maximum exposure of sample to attacking gases and acids.

I.B. Procedure for "Wet Chemical" Preparation of Sample Prior to Analysis

A 3 to 6 gram portion of S/C was accurately weighed (±0.005g) and dried for 6 to 24 hours at 40° to 50° C.

For comparison of the Pt and Pd yields from separate experimental "runs," accurate values of actual metals contents were needed. The results from "wet chemical" attacks upon all of the different S/C varieties were obtained. This was based on the assumption that all PGM metals content amenable to attack could be removed and determined by careful application of the separation and analysis techniques, and that PGM in the S/C samples could not be separated and recovered any more thoroughly by the combination
of gas-phase treatment and post-treatment rinsing. No evidence to refute the assumption was discovered.

"Wet chemical" (liquid-phase) attacks and separation of PGM content from S/C samples were made as follows:

An aqua regia mixture of 60 to 65% HCl and 30% HNO₃ (percentages by volume of concentrated acid to mixture volume) was used. A 3 to 6 gram sample was treated with 300 to 400 ml of aqua regia and heated to 60°-70° C. using intermittent magnetic stirring of the mixture.

The sample was cooled to 30°-35° C. and filtered through 2 circles of Whatman #1 filter paper, using "house" vacuum. Retaining the filtrate aside, the S/C sample was further crushed to an average particle size of 20 mesh or finer. This sample was again heated to 60°-80° C., in an additional 150-200 ml of aqua regia, for two hours. This mixture's filtrate was boiled at 90° C. or higher to reduce volume and to remove all dissolved NOx. Destruction of residual HNO₃ was aided by additions of 10 to 20 ml of concentrated HCl and at least two evaporations to a syrup of 15 ml or less volume. Cooling to 20°-25° C. and a final filtration through Whatman #1 paper concluded the separation.

I.C. Nature/Types of Samples Studied

Three varieties of supported catalyst were studied.
Each unit was an "oval rod" shape, typically 400 to 1000 grams, 150 to 250 mm length, and 100 to 250 mm width.

1. Chrysler Corporation's "Small Oval" Catalyst

Chrysler Corporation supplied a pair of catalytic converter oval blocks of a platinum-only catalyst type. Due to their size relative to a set of similarly shaped but larger volume blocks of a different nature, these were named "small oval;" the others, the "large oval blocks." Weight of the inlet member of the "small oval" set was 496.02 grams. Chrysler identified this specimen with the following data:

"oval #7476-149 (50/0), set 777-Boron fleet 48,212 miles (use)"

Data furnished by Chrysler claimed a platinum content of 0.47 grams per oval unit (new); this would be $9.27 \times 10^{-4}$ grams Pt per gram S/C.

C.2. Chrysler Corporation's "Large Oval" Catalyst

Chrysler also provided a set of road-used catalytic converter ovals bearing both Pt and Pd metals as catalysts, in a 70/30 ratio by weight. The inlet
member of the pair was chosen for study, and had a weight of 927±5 grams (Uncertainty originated from the process of cutting the block prior to an accurate weighing. The companion "outlet" oval weighed 927.45 grams.). The following data were furnished for this "large oval" block, by Chrysler Corporation:

"Set 381/U.O.P. 70-30 catalyst, 7471-175, Car 559, 49, 943 miles use." Reported loading of Pt and Pd totaled 1.555 grams per oval. This corresponds to 1.17 (±.01) x 10⁻³ grams Pt per gram S/C, and 0.50 (±.01) x 10⁻³ grams Pd per gram S/C.

C.3. Ford Motor Corporation's Catalyst

The Ford Motor Corporation supplied four monolithic/ceramic catalytic converter ovals. Two of these were new, and two had received road or simulated road use. For study, the "used" oval # H-317-305-1" was selected:

It was tested by F.M.C. 2/16/74 on "engine" XO-584-1-13." Net weight of the oval was 327.97 grams. No indication as to Pt and/or Pd content was offered with the units or accompanying letter.

II. Gas-Phase Treatment (Chemical Attack) of Catalyst Samples
A. Equipment

Tube Furnace

A Lindberg model/type 59344 console-54031 furnace combination was used, with an operating range of 400°-1200° C. The console was set for a proportional band of ±6°, with reset at 6 M/R.

Pyrometer

A digital read out pyrometer/indicating thermometer served for temperature measurement, with iron/iron Constantan alloy 10 gauge (AWG) thermocouples leading from the outside of the reactor tube (at 2 points). One point measured reaction temperature, with the other point measuring temperature of the out flowing gas/products stream.

Glass Reactor

The all-glass reactor system, as illustrated in Figure 1, consisted of the following components, from "upstream" to downstream end:

(a) A hand-blown Pyrex/Vycor adapter was connected to 3 incoming individual gas stream parts. The end connection was a 1" (25") O.D. Vycor male ball joint (18/8) used to couple with a corresponding opening on the reactor tube.

(b) The reactor tube was a quartz tube of 87 cm length, of 25 mm (1") O.D. and 0.2 cm wall thickness, which had a female 18/8 Vycor ball joint at each end.
ALL-GLASS REACTOR SYSTEM USED IN GAS-PHASE ATTACK OF CATALYST SAMPLES

Components of System:

(a) Pyrex/Vycor Inlet-Adapter with 3 limeglass ports to admit reactant & carrier gases

(b) Quartz Reactor Tube, 25mm O.D., 2.0 mm wall 870 mm long, with female 18/8 mm ball joints of Vycor (mid-section enclosed within furnace during run)

(c) Claisen Adapter, of borosilicate glass, with 18/8mm male ball joint of Vycor

(e) Gas Absorber/Traps, of borosilicate glass, (Ace Glass Co. #8746) with Nylon bushings and FEPFE O-rings; the one coupled to the adapter was filled with 10% (v/v) HCL, the other one with 6M NaOH (aq)

1 through 9, respectively, refer to openings in system upon dis-assembly and/or gas flow during operation.
(c) A Claisen adapter of borosilicate glass (Ace Glass Co.) was fitted with a male Vycor 18/8 ball joint to couple with the reactor tube.

(d) Spring-loaded metal clips maintained tension on both sets of 18/8 ball joints during each experimental "run."

(e) The downstream end of the Claisen adapter directed exiting gas flow into a tubular (38 mm o.c.) borosilicate glass gas absorber/trap (Ace Glass Co. assembly 8746). Polyethylene tubing (Tygon) of 13 mm ID carried gases from the side arm of this first trap of identical construction, prior to their venting into the fume hood.

(f) The first of the gas traps was filled to two-thirds of its capacity with 10% (v/v) HCl solution. The second trap was likewise filled with a 6M aqueous NaOH solution.

Post-Reactor Heating

An 18 mm width heating tape assembly and accompanying 110 volt powerstate-type transformer provided controlled heating of the exterior of the reactor tube, at an area of the tube "downstream" from the tube furnace's heating coils. This was provided to minimize condensation of any sublimates prior to the gas stream's entry into the first absorber.

Reactant Gases

"Commercial purity" nitrogen, carbon monoxide and chlorine gases were used, with no preliminary drying. Nitric oxide was provided from Airco lecture-size bottles
Gas Flow Quantitative Measurement

Rotameters served to measure gas flow volumes from the individual cylinders, with manual adjustment of the regulators to correct selected flow volumes. These rotameters were used:

(a) For N\textsubscript{2} measurement, a calibrated Brooks rotameter #1355-07C1AAA(#1) served for all runs.

(b) For CO measurement during all applicable runs, Brooks rotameter #1355-07C1AAA(#4) was used.

(c) For Cl\textsubscript{2} measurement, an air-calibrated Gilmore rotameter (model # not available) with a range of 0 to 300 ml/minute was used. Corrected flow volume of Cl\textsubscript{2} was calculated as follows:

True Flow Rate = 0.64 x Recorded Value (Rate)

0.64 is the quotient of (M.W. of N\textsubscript{2}) divided by (M.W. of Cl\textsubscript{2}), taking the molecular weight of nitrogen (N\textsubscript{2}) as equivalent to the average molecular weight of air.

(d) For measurement of NO flow, an air-calibrated Gilmore brand rotameter with a range of 0 to 300 ml (minute was used, with corrected NO volume (flow rate) calculated as (0.97) x (recorded flow rate).

Shaker Device

A Burrell flask/test tube shaker with angle settings from 5° to 8° was used, in sample work-up procedures.
II.B. Gas-Phase Treatment Procedures

In this discussion, a "run" refers to a complete sequence of the gas-phase treatment of a S/C sample: Sample loading into the reactor, followed by chemical attack of the sample with oxidizing gases at elevated temperature, followed by removal of the S/C sample and rinsing of any sublimed salts from the inner walls of the reactor tube, collection of the acidic solution in the first gas trap, and a shaking of the S/C sample with dilute HCl solution. A sample for each run weighed 3 to 6 grams, and was detailed from a larger portion of S/C as described earlier. Drying of each of the accurately-weighed samples for 6 to 24 hours prior to the run was performed, at 45° to 60° C. An objective testing of how this drying might improve performance of the reaction system, i.e. improve yield, was not done.

Preparations prior to a run were as follows:

The quartz reactor tube was thoroughly rinsed by both 10% HCl and deionized water, then dried. A tuft of Pyrex "wool" sufficient to block movement of dust or S/C particles but not hinder gas flow was pushed into the
tube to a depth of 15-20 cm. The S/C sample was carefully poured into the tube from the same end. A second "wool" tuft was added with gentle pressure to create a zone of S/C sample held 10-15 cm from the downstream end of the tube. Loading the sample at this location allowed for adequate pre-heating of the incoming gases before contact with the sample.

A thermocouple was attached to the outside wall of the reactor tube at the section in which the sample was located by means of heat-resistant tape. A second thermocouple was attached outside of the tube wall at its downstream junction (with the Claisen adapter). This thermocouple allowed monitoring of the temperature of the heating tape wrapped around that area of the tube.

With all equipment and the sample in place, a run's operation involved coordinated adjustments of gas flow and furnace temperature, as is described:

The flow of N₂ was commenced and closely monitored initially, with any signs of leakage or lack of outflow pressure within the system corrected. Insufficient lubrication of the 18/8 joints was an occasional problem. With proper flow, heating of the furnace was started. Upon an indication of desired reaction temperature being achieved, by means of the digital pyrometer read out, "starting" time was recorded, and the flows of chlorine and associated gas(es) were begun. Often three to five minutes would be required to adjust those flows to desired level, due to a tendency for flows to drop.
At the end of the desired 2 to 9 hour run length, flows of oxidizing gases and power to the furnace were simultaneously stopped, with \( N_2 \) flow continued until the reactor tube temperature dropped to 50°-75° C. Power to the heating tape was usually stopped 15 to 30 minutes after the run itself was stopped. With the furnace temperature lowered, a bleed line from the \( N_2 \) regulator was opened, and \( N_2 \) directed into the \( Cl_2 \) line just downstream of the \( Cl_2 \) rotameter, to flush all remaining reaction gases from the reactor tube and adapters.

With no gas flow and furnace temperature close to room levels, processing and removal of the S/C sample was accomplished:

The reactor assembly was carefully taken apart to avoid contamination of the tube's inner wall surface or other areas possibly bearing sublimates from the reaction. Using a wash bottle with a 5% HCl solution, the inside wall of the reactor tube downstream of the plug holding in the S/C sample was rinsed, with the drippings collected for later analysis. The Claisen adapter was similarly rinsed.

The "wool" plugs, plus S/C sample, were pushed from the tube into a flask by means of a long brass rod (contact with iron containing materials could affect later analytical values). This material was the "residue;" the solution derived from it was likewise deemed the "residue" sample from the run, after the rinsing of this S/C material.
The residue was added to an Erlenmeyer flask, along with a standard amount of 10\% (v/v) HCl -- 100 ml per 5 grams of sample. The resultant slurry was shaken for 30-35 minutes with a Burrell shaker so as to dissolve any non-volatile PGM compounds still in the S/C material. Following shaking, the slurry was heated to 60°-70° C. for 40 to 60 minutes. The slurry was cooled to 40°-60° C. and vacuum-filtered through 2 discs of 55 mm Whatman #1 filter paper. This separated all but the finest support particulates in 7 to 10 minutes.

The solution from the first gas trap was carefully removed and transferred to a beaker or Erlenmeyer flask, with the absorber/ trap tube and lead-in arm rinsed at least twice with deionized H₂O, these rinsings added to the "trap" sample. This trap sample frequently was heated to 60°-70° C. for a period sufficient to reduce its volume to a level comparable to that of the "residue" or "tube rinse" samples.

The residue sample for a run was always analyzed separately. For some runs, separate determinations of the PGM were made for the tube rinse, the adapter rinse, and for the trap (rinse). A few runs involved a collective analysis from combined rinses. Others included determinations of the residue, tube, and (adapter trap) rinse, etc. Such variations were to observe any patterns of special distribution of product sublimate which might be happening.
III. Sample Analysis

A. Equipment

Aside from glassware common to most analytical chemistry labs, several apparatus of specialized nature or selected quality were necessary for sample preparation or analysis:

Spectrophotometer

Colorimetric measurements were made with a Bausch and Lomb Spectronic 20 visible/near IR spectrophotometer, adjusted for absorbance and transmittance readings at 525 nanometers. Absorbance levels of 0 to 0.5000 units were read from the instrument's meter and recorded directly; above A of 0.5000, the % transmittance value was recorded, with subsequent calculation of absorbance.

Liquid/Liquid Separation Funnel

A Squibb-type extraction funnel of 125 ml volume served in the extraction of iron impurities from samples, via cupferron chelation.

pH Measurement

A Markson "Electromark" pH/conductivity analyzer with Polymark electrode was used in all pH measurements, with digital read out to ±.01 units. Prepared and standard solutions of pH 7.00 and pH 4.00 served in the standardization and adjustment of this meter; these standards were from Fisher Scientific.
Cooling Bath

An electrically-powered cooling bath system allowed rapid immersion and cooling of heated volumetric flasks prior to analysis of their contents. A temperature of $20^\circ$ C. ±$1^\circ$ C. was maintained.

Volumetric Glassware

The volumetric flasks and pipets used in this study met NBS "Class A" standards.

III.B. Reagents

All chemicals used in this study's analysis were ACS Reagent or J. T. Baker Company's "Analyzed Reagent" standards, except where noted. Beyond the solutions of NaOH, HCl, etc., specific reagents necessary to the study were:

p-Nitroso-N, N-Dimethyl Aniline

Solutions of the colorimetric agent, p-nitroso-N, N-dimethyl aniline, were prepared by addition of 5-10 ml of absolute ethanol to a 100.0 ml volumetric flask, followed by 0.50 grams of reagent, then slowly filling the flask to volume, interrupting this to shake the flask and hasten dissolution of the reagent. Eastman "purified" grade p-Nitroso-N, N-dimethyl aniline was used. A dark green to olive solution was the result. Hereafter in this report, the colorimetric reagent will be referred to by the abbreviation "NDA."
Cupferron Reagent

Eastman "purified" grade cupferron was used as an agent for the separation of iron from samples, prior to their colorimetric analysis. A solution of 1.5 grams cupferron per 25 ml deionized H₂O was prepared on each lab date for analysis.

Buffer Solution

A buffer solution of pH 2.2±0.2 units served to insure maximum color development of the NDA-Pt and NDA-Pd absorbances. Preparation involved the addition of 53 to 60 ml of 1M HCl. pH monitoring was used to reach the specified pH value.

From this buffer, a 10-to-12 fold dilute wash solution was prepared for rinsing, in preparation for each sample's determination.

III.C. Procedures for Determination of Platinum and Palladium

1. Treatment for Iron Contamination in Sample

All "residue" and most "rinse" samples were believed to contain concentrations of iron which could significantly alter values for Pt and Pd determination. Therefore, all runs used in preparation of data for this report, 1007 to 1331, inclusive, involved cupferron pretreatment of each sample for iron removal. Cupferron
chelates iron selectively from aqueous solution; the "iron cupferrate" complex is selectively soluble in chloroform, whereas Chlorides or related compounds of Pt and Pd possibly existing in the sample are insoluble in chloroform. Samples were treated in the following manner:

pH was adjusted to 1 or lower, by addition of concentrated HCl. The sample was added to a 125 ml Squibb funnel, and was followed by a volume of U.S.P. or reagent-grade chloroform equal to 1½ times sample volume. Next 5 to 6 ml of a 40% cupferron solution were added. The sealed funnel was vigorously shaken for 1 minute by hand. Within seconds following the complete separation of the CHCl₃ and aqueous layers, the brown layer of CHCl₃ was drawn off carefully (free of trapped aqueous layer bubbles) and discarded. The addition of fresh CHCl₃ followed, repeating the 1½ volume formula, and vigorous shaking followed. If the second complete layer of CHCl₃ drawn off was yellow or brown, the addition of CHCl₃ was repeated. The CHCl₃ layer was colorless upon separation of all iron cupferrate from the aqueous layer.

Each sample was readjusted to a pH of 2.2±1 units with dilute (0.1 m to .2 m) NaOH, and diluted to volume in a suitable volumetric flask. Usually 25.0, 50.0 or 100.0 ml, this solution was termed the sample's "master" volume, for reference in its dilutions.
C.2. Colorimetric Analysis Based on the NDA-Pt and NDA-Pd Complexes

The colorimetric procedure selected for the determination of platinum and palladium was proposed in 1954 (37), when a family of reagents which react readily at room temperature with minute amounts of Pd were found to also react with Pt. The reaction with Pt, and to a lesser degree, with the other four PGM occurs only at elevated temperature, such as by heating solutions bearing these metals to 80°-100° C. over 20 to 60 minutes. The resulting absorbance of light due to Pt reagent and Pd reagent is additive, so that
\[ A(\text{Pt Pd, at } 80°-100° \text{ C.}) - A(\text{Pd, } 25° \text{ C.}) = A(\text{Pt}). \]

The agent para-nitroso-N, N-dimethyl aniline was selected for use in this study because of its commercial availability and solubility in both water and ethanol. This reagent has received attention by other PGM analysts since its introduction (39). A linear absorbance over 0.7 - 2.5 p.p.m. was reported for Pt and a similar range of 0.2 - 1.0 p.p.m. was cited for Pd determination (37, 38).
This method gives readings of maximum absorbance for the Pt complex at 525 nanometers wave length; iron complexes can seriously interfere at this same wave length (39), and must be removed from samples prior to their colorimetric analysis. The use of cupferron to chelate the iron and allow solvent extraction was a routine precursor to the analysis. Other species such as aluminum complexes present in solutions from the gas-phase stripping of platinum from the S/C samples were not cited as positive interferences by earlier researchers (37, 39).

In planning for each determination, a rough estimate of Pt and Pd contents was made for the "master" solution of that sample, in terms of "p.p.m." (mg. metal ion per liter). It was desired to prepare at least 6, and preferably 8, aliquots of identical concentration per sample. Multiple aliquots were analyzed for the following reasons:

One, to be able to calculate a more accurate average concentration from the determination; two, to provide for duplicates should one or more aliquots be lost during the procedure from contamination or breakage.
The desired concentration ranges for the aliquots were related to the estimated ranges in the master sample, and appropriate dilutions made, always using volumetric pipets and flasks. For example, in making up a set of aliquots using 25.0 ml volumetric flasks, the volume of the other added chemicals (buffer and NDA reagent) dictated a practical limit of 10 ml of "master" solution per aliquot. Filling flasks to over two-thirds of their capacity presented difficulties during the color development of the NDA-Pt complex. Filling to volume was done after the heating necessary to color development.

With exceptions noted, the originally-proposed procedure (37) was followed in the determinations of Pt and Pd concentration in the samples:

(a) 5 ml of the pH-adjusted buffer were added to a 50 ml volumetric flask.

(b) 1 ml of a 0.5% solution of NDA was pipetted into the flask, followed by several drops of deionized water, as needed, to wash and NDA splashed onto the inside wall of the flask neck.

(c) Addition of a 1.0 to 25.0 ml volume of sample was made. 5.0 to 25.0 ml were preferred for sufficient accuracy, balanced against over-filling of the flask prior to color development.
(d) 10 to 20 ml of the dilute buffered wash solution were then added to bring the aliquot's level to 33-35 ml.

(e) The aliquots of a sample only being measured colorimetrically for Pd are filled to volume with deionized H₂O. (This is in variance with the original literature, which recommended use of 95% EtOH for this purpose.)

(f) For each aliquot of the sample to be color-developed for Pt determination, an identical aliquot, minus sample addition, was prepared. These served as "blanks;" one was brought to volume without heating, and served in the adjustment of the Spectronic 20 to 100% transmittance prior to readings of "Pd only" absorbance. The other "blank" aliquots were "color-developed" simultaneously with those for determination of "Pt + Pd."

(g) With the Spectronic 20 set at 525 nanometers and the calibration to "100% T" for the non-color developed blank's reading made, the instrument was ready for accurate measurements of absorbance due to the Pd-NDA complex. Prematched cuvettes, or the same cuvette (with thorough rinsing with both acetone and de-ionized H₂O between each reading) were used.

For each reading of absorbance of an aliquot's solution, 1 to 3 ml of the aliquot's solution was poured into the cuvette, this was poured out, and then the 4 to 6 ml of solution to be measured added. Following the reading's recording, the sequence of acetone, de-ionized water, and sample rinsing was followed, prior to the reading to the next sample.

(h) Prior to their readings for absorb-
ance due to Pt plus Pd complexes, half of the aliquot flasks were heated to 100° C for 23 minutes. The flasks for heating each had a lead metal "collar" added, to prevent their "tipping-over" due to occasional super-heating of the bath. The bath was a 1000 ml beaker one-third to half filled with tap water. The flasks were removed after the 23± minutes and immediately transferred to a cooling bath maintained at 20° C.

(i) After 5 minutes in the cooling bath, the aliquot flasks, both "blank" and sample-containing, were removed, and filled to volume with de-ionized water.

(j) The 1 to 4 color-developed blanks were combined into 1 beaker-or flask-full of solution, and a portion from it used to adjust the Spectronic 20's % transmittance reading to 100%.

(k) The sample-containing aliquots were measured for their absorbances within 10 minutes of being filled to volume, similar in manner to the sequence given in (g).

III.C.3. Advantages of Chosen Procedure, Using NDA Reagent

The nature of the sample solutions obtained from "work-up" of the gas-phase reaction's products suggested the application of a spectrophotometric technique as the most convenient route for measuring the low concentrations of PGM expected to be present in the catalytic converter units. Usage of the NDA reagent for
colorimetric determinations was the exclusive choice in this study, based on the following points:

(a) It showed high sensitivities for both Pd and Pt complexes which would allow the determination of both the very low concentrations and much higher concentrations (by appropriate dilutions). For example, samples of 3 to 6 grams with 0.3-0.5% (by weight) of Pt + Pd were routinely analyzed, along with traces of these metals that were 50-100 --- fold more dilute (e.g. rinses of sublimates from the gas-phase catalyst attacks).

The original researchers of the technique reported "practical" sensitivities for Pt and for Pd, respectively, as 0.1015 p.p.m. and 0.0067 p.p.m., in 1 cm path cells (37). They reported ranges of Beer's Law obeyance as 0.7 to 2.5 p.p.m. for Pt, and 0.25 to 1.00 p.p.m. for Pd (37).

(b) Use of visible/near IR-long UV range units such as the B & L Spectronic 20 provided an economical alternative to more expensive and skilled-labor-intensive devices such as optical spectrography, enabling greater and wider potential application for industrial analysis.

(c) The additive absorbance scheme for measuring concentrations of Pt and Pd from separate aliquots of the same sample eliminated a need for additional reagents, dilutions to significantly different concentrations and other labor-intensive operations.

(d) The problems of interference by base metals or anions resulting from chemical
attack were easily controlled, with the serious problem of iron contamination completely eliminated by cupferron chelation (38).

(e) Where the concentrations of either Pt or Pd relative to the other were significantly different relative to each other, there was available the option of quantitative extraction of the NDA-Pd complex at room temperature from the yet uncomplexed Pt ion (39).

(f) The original paper on additive absorbance analysis of Pt + Pd mixtures claimed attractively low values for "% standard deviation" -- 1.0% for Pd, and 1.5% for Pt, when the metals were measured with the concentration ranges of maximum color development and optimum pH.
RESULTS

I. Reaction Variables/Parameters Under Study

Initially, both the conditions necessary to promote the desired reactions and the possible physical and chemical products of the proposed system were quite unclear. Nineteen "runs" of the system apparatus were initially studied for qualitative and quantitative evidence of PGM compounds, as well as how a wide range of several variables influenced the "evidence."

A choice of three main variable parameters was made, and another 40 "runs" carried out, studying samples from two types of PGM bearing catalytic converters. Temperature, time and reactant concentrations could be varied in a controlled manner, with reproducible yields and effects.

Temperature was deemed the most significant variable in determining yields. A range of $350^\circ$ to $1025^\circ$ C. was studied, using $100^\circ$ increments in most runs. $350^\circ$ C. was the lowest practical temperature.
for furnace operation and 1025° C. was selected as the upper limit. Literature documentations of the existence of volatile PGM species over 300° to 800° C. and projected lower energy and reactor materials costs evoked most interest in the lower end of the range. Preliminary evidence of a high volatility for Pt and Pd species above 800° C. prompted a number of runs at 900° C. and 1025° C.

Chlorine gas was utilized as the main oxidizing agent for all runs; carbon monoxide was selected as the co-reactant for most runs, with nitric oxide and chlorine used during a few selected runs. Considering the ratio of Cl₂ flow volume to that of its co-reactant gas, the ratio "R" can be stated for each run for purposes of comparison, i.e., \[ R = \frac{\text{Cl}_2 \text{ volume}}{\text{co-reactant volume}} \]
where all volumes were in cubic centimeters per seconds.

For runs using Cl₂ plus CO, the "R" range was 0.90 - 3.04, with most runs at "R" = 1.68 or 3.04. Four runs using Cl₂ plus NO involved a ratio of 2.80 or 5.27.

The influence of varying ratios of the N₂ carrier gas to chlorine or combined reactants was not considered.
A number of runs identically conducted except for the time of reactant gas flow were studied for both types of S/C samples. Periods of 2, 4, and 6 hours were considered in these runs. Original intentions to study the effects of up to 10 hours of reactant flow were abandoned early in the project due to an emphasis on temperature and reactant concentrations over time, as well as the impracticality of extended laboratory hours. See Tables I plus II, Appendix A.

II. Standards for Product Yield Evaluation
   A. Calculation of PGM Content in Samples

Data provided by Chrysler Corporation and Ford Motor Company established an initial idea of how many and how much of the PGM were originally added to the supports. The possibility that their figures might lack accuracy or that some of the metals were partly or completely removed during catalytic converter operation prompted the wet chemical stripping of any PGM amenable to such attack and the use of "used" converter ovals instead of new units.
A nine-step sequence of calculations was used to arrive at values for the contents of platinum and palladium upon samples initially treated with either the gas-phase or wet chemical/liquid-phase methods, as is more fully covered in Appendix C. In brief, known concentrations of Pt and Pd were complexed and corresponding absorbances recorded. Preparation of accurate working curves and definitions of precision over various portions of those curves in turn allowed measurements of samples treated by the liquid-phase method. Values for the Chrysler catalysts were accurately determined, as were those for the Ford catalyst; the latter catalyst proved to contain both Pt and Pd.

II.B. Values for PGM Content in the Small Oval Chrysler Catalyst

No evidence of palladium content in this type of catalyst was found. The determinations of Pt content led to a value of 1.14 (±0.15) x 10^-3 grams per gram of S/C. Determined by spectrophotometric analysis of solutions bearing all Pt content of the samples, this was accepted as the actual content, for all comparisons of Pt yield via the gas-phase treatment.
II.C. Values for PGM Content in the "Large Oval" Chrysler Catalyst

Liquid-phase treatment and determinations for Pt and Pd content resulted in values for Pt at 1.12 \((\pm 0.12) \times 10^{-3}\) grams per gram S/C, and for Pd at 0.48 \((\pm 0.05) \times 10^{-3}\) grams per gram S/C material.

II.D. Values for PGM Content in the Catalyst Tested from the Ford Motor Company

Samples from the Ford oval unit \#H-317-305-1 were determined to show an average value of 1.75 \((\pm 0.31) \times 10^{-3}\) grams Pt per gram of S/C material, and a content of 0.94 \((\pm 0.06) \times 10^{-3}\) grams Pd per gram S/C. This led to a conclusion that the catalyst was originally a 65/35 or 70/30 Pt/Pd type, similar to the large-oval catalyst furnished by Chrysler Corporation.

III. Physical/Chemical Results - Qualitative Observations

A. Flows of Reactant Gases

The flows of oxidizing reactant gases within the reactor were evidenced by the green to orange fog during a run, as well as by the constant bubbling of the exiting stream through both gas traps. The flow
was noticeably paler or colorless in the reactor's middle section at all elevated temperatures and particularly above 800°C.

III.B. Optimum Sample Exposure to Chemical Attack

Yields from the first series of runs were low, i.e., 0 to 50%. All involved exposure of the sample to the gas flow with the S/C material in a porcelain combustion boat. Several runs involved addition of aluminum chloride powder in an attempt to increase yields. Results were still poor, and no visible, colored "zones" of product sublimate were observed downstream within the reactor or on the inside wall of the adapter.

An alternate method of exposing the S/C samples was selected; its use resulted in an immediate increase in yield of sublimed products and in a brown-orange zone of sublimate downstream of the sample, on the inside wall of the reactor tube. This was referred to a "plug flow," and has been described in the Experimental section. This first run with "plug flow," #1007, involved a Cl₂ plus CO reactant gas combination.
Apparently, use of the combustion boat offered insufficient surface area of S/C for the reaction, although the reason was not understood or investigated.

III.C. Sublimates and Products from A Run

Sublimates downstream of the sample-located section within the reactor tube were observed for all 40 runs using plug-flow treatment of samples.

Without addition of the heating tape near the junction of the reactor tube and Claisen adapter, the sublimate band was usually 3-8 cm. long and dark-orange to brown, and virtually opaque. Such bands were well formed within the first two hours of a four hour run. During run 1101, which involved use of an unusually high level of CO relative to Cl₂, the band color was a lighter auburn to yellow; whether this was caused by a lower amount of sublimate or by the presence of a different PGM complex was not investigated, but was peculiar to the low Cl₂/CO ratio.

Use of the heating tape resulted in a sizeable decrease of color intensity and more translucence of
the sublimate bands; they were located along the adapter's inside/inner wall, especially on the outer (top-most) curve, with the remainder of the adapter's inside wall usually "frosted" with a light yellow to lemon shade of sublimate.

These yellow to brown sublimates may have been anhydrous or unstable to moisture, as they usually reacted exothermically upon contact with the rinse solution during product recovery. Care was taken to spray rinse solution into any vapors from such contact, to lessen minute amounts of vaporized Pt or Pd species escaping. Another result of the "hydration" reaction was often a slightly lighter yellow "foam" within the adapter or gas trap lead-in tube. One instance of exposure to laboratory air (of a freshly-completed run's adapter) over about 36 hours resulted in a "lemon meringue pie" topping simulated within the adapter.

Preparation of rinse sample solutions suggested on several occasions the presence of aluminum ion within the solutions; the required adjustments of
pH prior to analysis (using NaOH) resulted in transient formation of a white colloid over pH 6½ to 8½. A volatilization of alumina as AlCl₃ during the runs is suggested, in view of the aluminum ion's amphoteric nature. Such behavior also suggested that the catalyst support was not wholly inert to the proposed gas-phase reaction system.

IV. Physical/Chemical Results - Quantitative Observations

A. Distribution of Volatilized Products

A major objective in the study was to maximize the degree of reaction product volatilization and separation from the sample matrix. Complete separation was not achieved in any run, but degrees of such separation varied widely. Platinum and/or palladium content within all samples was assumed, and all but a handful of samples did contain Pt and Pd (or Pt alone).

Tables I and II present the conditions of operation for the 40 runs featuring plug flow location of the sample. Tables III and IV cover these same runs' results — each is described in terms of the percentage
of Pt (and Pd) content on the sample which was converted to compounds amenable to determination. In this study, the small scale of operation dictated that all recovered PGM be used for such determinations. Commercially, these solutions would be directed to a separate in-plant recovery unit or prepared for delivery to an outside refiner.

The residue solution was analyzed separately for each run. Four combinations were used, with regards to collection of rinse samples from each run; these have been labeled I, II, III and IV; and a presentation of data regarding types II and III is found in Tables V and VI, Appendix B.

These combinations were:

I - The rinse of the reactor tube only; with the rinses of the adapter and of the first gas trap maintained and analyzed separately.

II - Rinses of the tube and the adapter combined; trap rinse analyzed separately.

III - Tube rinse analyzed separately; adapter rinse and trap rinse analyzed together.

IV - All rinses combined and only one analysis necessary.
In the determination of values from runs involving small oval Chrysler samples, type III was the combination used. This was due to the fact that most of the earlier runs didn't involve use of the heating tape and resulted in a heavy layer of sublimate within the reactor tube. It was assumed that a large difference between temperature existed between tube interior and adapter interior, and the experimenter was curious as to how much of the volatilized product would remain in vapor form at such lowered temperatures. With one exception, about 66 to 98% of all volatilized Pt was found in the tube rinse. The use of heating tape made little difference in such relative distributions.

Six runs involving large oval Chrysler catalyst samples had rinse samples collected in the type III manner; one run (#1113) found as little as 54% of the "rinse" Pt in the tube section, with three others showing less than 90% of the sublimed Pt in the tube rinse. The yields of Pd did not parallel those for Pt in the same runs, and percentages of Pd carried over into the adapter and trap were larger.
The relatively-greater volatility of the sublimed Pd species showed in the values for type II runs with large oval Chrysler catalyst samples; the rinsed contents from the first traps were analyzed separately from the combined tube plus adapter rinse. In 3 of 4 such analyzed runs (1315, 1317, 1313, 1310) 3 to 18 times as much Pd as Pt was carried over into the trap. Such behavior was not expected in view of the published reports on Pd halides and Pd carbonyl halides cited in the Introduction, and might justify elemental analysis in future work in this area.

IV.B. Yields from the Chlorine Plus Carbon Monoxide Treatment of the Small Oval Chrysler Catalyst

1. Effects of temperature variability

Using Chrysler's platinum-only catalyst, the relationship of temperature to metal yield received much attention, with 7 runs featuring a 4 hour reaction time and a set ratio of 1.68 for chlorine to carbon monoxide volume flow. Data from one of the runs was deleted from final consideration (#1011, conducted at 600° C.) due to unexplained variance of its data with that of runs made at lower and higher temperature (see
Table VII for specific data on this series).

Figures 2.1 (Appendix D) and 2.2 present the relationship of platinum yields via volatilization and overall chemical attack versus reaction temperature for the 6 runs under study.

Volatility and rate of chemical attack increase sharply from 700° C. to 900° C., decreasing somewhat above 1000° C.

![Fig. 2.2 Pt Yield versus Temperature for Pt only Catalyst's Treatment](image)

A gas flow of N₂ plus Cl₂, with no co-reactant gases also showed an increase of Pt compound volatility with temperature increase:

- Run 1050, at 450° C. - 2.0% of Pt in Rinse
- Run 1118, at 900° C. - 25.0% of Pt in Rinse

Both values refer to percentage of Pt in sample.
IV.B.2. Effects of Cl₂/CO Gas Concentration Variability

The relationship of the ratio (by volume) of Cl₂ to CO concentration was studied in 4 runs, all at 900°C over 4 hours, as this appeared to provide higher yields of Pt than lower temperatures. Table VIII, Appendix D, provides specific data. The sequence of Cl₂ % relative to CO % went as:

- Run 1118 (100% Cl₂) → Run 1202 (85% Cl₂)
- Run 1202 → Run 1303 (75% Cl₂) → Run 1024 (63% Cl₂)

The use of 75% Cl₂ gave best overall yield of Pt as well as best total attacked Pt, with Run 1024's use of 63% Cl₂ trailing slightly (54.7% of all available Pt found in rinse). Notably, run 1303's overall yield of 95.6% Pt was the best for all runs using the small oval catalyst.

It is suggested that for this type of catalyst, the 75% - 5% range for chlorine relative to carbon monoxide may be an optimum, if testing at several other temperatures at 2 to 4 hours shows similar yields.
IV.B.3. Effects of Time of Reactant Gas Flow

A set of 3 or more runs' data where all variables were held identical except for gas flow time is not available for comparison. However, 3 pairs of runs involving samples of the small oval Chrysler catalyst have been considered as to the effects of gas flow time upon platinum yield. Sets of 3 or more runs data would be more desirable in determining an optimum flow time for the process.

Runs 1024 and 1025 were each conducted at 900° C. with 63% Cl₂/37% CO flows. After 2 hours, the sample in 1024 yielded 54.7% of its Pt in the rinse portions, and 73.7% of all available Pt in the combined determinations. After 6 hours, 1025's sample had only yielded 84.8% of its Pt in the combined determinations, so three times the length of flow didn't improve yield dramatically.

At 1025° C. and the 63% Cl₂/37% CO gas flows, 2 hours (run 1216) yielded 45.4% of all Pt (in combined fractions), with 4 hours (run 1026) giving 48.0% of the available Pt.
At 700° C., a 2 hour run (#1327) had a greater yield of Pt in both the rinse and the residue fractions than did a run over 4 hours (#1324), or 58.0% total Pt content versus 24.2% total Pt. (Duplicate runs would be advisable before concluding what effects time had in reversing yields.)

IV.C. Yields from the Chlorine Plus Carbon Monoxide Treatment of the Large Oval Chrysler and Ford Catalyst (Bearing Pt plus Pd)

1. Effects of Temperature Variability

The important possible effects of temperature upon yields of Pt and Pd received attention in several runs. Six runs involved identical gas flows and concentrations, sample types, and reaction times (4 hours). Temperatures ranged from 350° C. to 1025° C.; specific data is located in Table IX, Appendix E.

Relationships of Pt and Pd yields to temperature are specifically graphed in Figure 3.1, see Appendix E, and that of the percentage of available Pt attacked and volatilized (in "rinse") is shown in Figure 3.2. Pt was not significantly attacked and volatilized over the 350°-600° C. range, but above 600° C., the amounts
increased rapidly, with no decrease over the 900°-1025° C. range. Conceivably, some maxima above 1000° C. could be determined. Pd volatility paralleled that for Pt up to 800° C., then dropped off to 4% by 1025° C.

Figure 3.2- Pt Yield Versus Temperature for Pt+Pd Catalyst's Treatment

A pair of runs over 6 hours time and at the 63% Cl₂/37% CO concentration level allowed a comparison between the effects of 450° C. (run 1122) and 900° C (run 1120). Both showed similar recovered Pt levels in the rinses (1.20% and 1.62%, respectively), but the levels of Pt in the residue portions were markedly lower at the higher temperature.

No analytical error could be held accountable. Repeats of this set of conditions at the 6 hour level
might help to determine if some reversal of Pt's oxidation was in effect. The same set of data showed an increase of overall recovered Pd with an increase in temperature (46.4% overall Pd yield at 450° C. and 76.3% Pd at 900° C) but a minute decrease in Pd carried away from the attacked sample by sublimation (3.5% versus 2.3%).

IV.C.2. Effects of Cl₂/CO Gas Concentration Variability

The more effective concentrations for Cl₂ and CO in the attack of Pt and Pd bearing S/C samples were different from those for the platinum -- only S/C samples. No sets of 3 or more runs identical except for the Cl₂/CO ratio were made with the Pt and Pd catalysts; several selected pairs of runs using such catalyst samples and identically conducted except for the ratio of Cl₂ to CO will be discussed. Table X, Appendix E, details yields from these pairs.

For runs 1108 and 1315, both conducted at 600° C. over 6 hours, the higher CO concentration of the former yielded higher overall levels of attack upon the catalyst's Pt and Pd, i.e. 93.2% Pt versus 73.9%
Pt. In fact run 1108 involved the highest yields of platinum of all Chrysler large oval catalyst samples (using the Cl₂ + CO mixture), and a rather good yield of Pd relative to other conditions.

Overall Pt yield and Pt volatility were also greatly increased by CO level increases in Run 1317 (37% CO) relative to run 1313, with only 25% CO. Pd yield dropped slightly with the increased CO levels (50.8% overall, versus 54.0% overall). But Pd in the residue portion sample was only 35.2% (of available Pt) for run 1317, and 50.5% for run 1313. The possibility that higher CO levels might increase Pt volatility but retard Pd volatility occurred to the experimenter but was not explored in this study directly. Industrially, Pt recovery might receive higher priority than Pd's due to economics; most likely, a compromise in conditions favoring both metals stripping would have to be sought.

At 900°C and 4 hours run time, a higher CO concentration for run 1128 resulted in a lower overall yield of Pt than obtained with the 75% Cl₂/25% CO
used in run 1306. (21.5% Pt versus 29.6% Pt) Pt rinse yield increased little with increased CO concentration (9.3% Pt versus 4.3% Pt) Pd overall yield increased slightly, with no increase in volatilized product, with increased CO levels.

Two runs with Ford catalyst samples suggested that its nature might be different in some way from that of the similarly-loaded (metal values both about 70% Pt and 30% Pd) large Chrysler S/C.

With both runs conducted at 850°C. over 6 hours, run 1331's lower CO level (25% of reactant volume) resulted in over twice as much overall Pt yield as in run 1129 (37% CO), and a similar increase in Pt volatility. Palladium behavior was opposite Pt's so far as volatility - the higher CO level meant 76.7% of available Pd in the rinse fractions, versus 60.4% with 25% CO in the reactant mix.

At 850°C., over 98% of both Pt and Pd contents in both runs was either volatilized or unavailable in the residue portions. Lack of time prohibited further runs with this potentially-interesting catalyst and set of conditions.
IV.C.3. Effects of Time of Reactant Gas Flow

Results from comparisons of several pairs of runs identical except time of reaction are not uniform; no sets of 3 or more runs identical except for time were conducted. It does appear that runs over 2-4 hours long were not conducive to higher Pt or Pd yields; most extended runs saw some reversal of equilibrium as regards Pt volatilization and attack. Pd was continuously but slowly attacked for the duration of all runs. Data from 4 "pairs" of runs differing only with respect to reaction gas flow time are presented in Table XI, Appendix E.

Runs 1313 (2 hours) and 1310 (6 hours) were conducted with the 75% Cl₂/25% CO flows and at 800° C.; increased run time did produce increases in overall Pd and Pt yield. Volatilized Pt and Pd also increased with run time, with Pd's change being most effected — 3.54% versus 20.4%.

IV.D. Yields of Platinum and Palladium from the Chlorine Plus Nitric Oxide Treatment of the Large Oval Chrysler Catalyst
The use of NO in place of CO received attention in 4 runs; three of these runs' samples were analyzed and their values compared as to the effects of temperature and relative gas concentrations. Specific data are listed in Table XII of Appendix F.

A usage of 900°C in run 1211 resulted in a sizeable increase in Pt's volatility relative to that at 700°C (run 1206), even though total Pt yield actually dropped for the higher temperature run. Pd's behavior was quite similar; values for 600°C and 800°C would be desired before drawing firm conclusions.

For runs 1212 and 1211, both at 900°C, the higher Cl₂ concentration in 1211 appeared to greatly enhance overall Pt attack and Pt compound volatility, but decreased volatility of Pd (8.23% from 26.7%).

Table XII also compares yields of Pt and Pd to those from similar runs using Cl₂/CO instead of Cl₂/NO. The NO co-reactant resulted in sharply higher yields of Pt, and significantly higher Pd yields.

IV.E. Comparative Yields from Large and Small Oval Chrysler Catalyst Samples Under Identical Treatment Conditions
Several pairs of runs involving identical operating conditions but different catalyst types have been compared. Specific data are furnished in Table XIII, Appendix G.

Of 6 such pairs, 4 show that similar treatment yielded higher levels of chemical attack and recovery of Pt in the small oval (Pt-bearing only) catalyst. Only at 1025° C. and 350° C. were the large oval catalyst samples attacked more efficiently. At a temperature of 350° C., with a 1.69 Cl₂/CO ratio and 4 hours reaction time, 84.3% of available Pt on the large oval sample in run 1113 was attacked, while only 62.6% of available total Pt on the small oval catalyst sample was attacked. Volatility of Pt was poor for both samples at the lower temperature.

At 900° C. over a four hour run period with a 1.68 Cl₂/CO gas flow, chemical attack of the small oval catalyst sample in run 1024 was an overall 73.7% for Pt, versus 21.5% for Pt in run 1128's sample. At 1025° C., the large oval catalyst sample in run 1218 was attacked more efficiently than the small oval catalyst in run
1026 (65.3% total Pt versus 48.0% Pt).

It is believed that sufficient excess of Cl\textsubscript{2} volume flow existed to rule out this disparity based on the "added" Pd content "using" so much of the Cl\textsubscript{2} as to deprive the Pt of sufficient reactants. It is more plausible that Pt and Pd chemistry in some ways contradict each other with respect to kinetics or other equilibrium influences.
CONCLUSIONS

I. Treatment Process

Both platinum and palladium, as metallic "fines" and salts, can be stripped from their ceramic-type supports in the automotive catalytic converts by the promoted gas-phase attack of chlorine or by a combination of the gas-phase attack, followed by liquid-phase rinsing of the soluble salts.

Platinum and palladium behave differently in their response to such chemical attack under identical conditions (e.g., temperature, pressure, relative concentration of the metal in the matrix). Platinum was found to behave differently when in combination with palladium than when it is present alone in comparable matrices and under identical conditions of chemical attack.

The gas-phase chemical attack upon Pt and Pd at lower temperatures, e.g., 300-600° C., may be as efficient (oxidized salt yields) as at much higher temperatures, but in practice, the volatilities of any re-
sultant complexes with chlorine and carbon monoxide or nitric oxide are not analytically or economically significant below 700-750° C. A temperature of 800-900° C. appears to be the maximum range for such volatile complexes.

The Cl₂ + NO system appeared to offer higher yields for Pt and Pd at a given temperature, relative to Cl₂ CO. However problems due to the corrosion of stainless steel or other metallic handling equipment (e.g. rotameters) are also significantly higher for this system.

For the small oval Chrysler catalyst, loaded with Pt only:

- Best volatility of Pt complexes and best rate of chemical attack upon Pt appeared to be at 800-900° C.

- The lower concentration of CO at the 3.04 ratio (Cl₂/CO) versus the 1.68 ratio favored chemical attack of the platinum.

For the large oval Chrysler catalyst and Ford catalyst, both loaded with Pt and Pd:

- Maximum or best levels of chemical attack of Pt were at 450° to 800° C., but with highest volatility for its complex with Cl₂ and CO at 900-1025° C.
- Maximum levels of Pd chemical attack and of complex volatility were at 700°-900° C.

- Platinum in such catalysts was attacked to a greater extent at higher CO concentrations (lower Cl₂/CO ratio) than at lower concentrations. This was contrary to its behavior in the Pt-only catalyst.

- Under the conditions established for experimental study, a 2 hour reaction time was sufficient. It was observed that for reaction times over 4 to 6 hours, some previously-volatile Pt might have been reduced and rendered unavailable for analysis. For Pd no such reversal of equilibrium occurred — longer reaction times yielded more Pd salts.

The tendency for recovered palladium salts to be concentrated further along (downstream) the reactor tube system suggests that the complexes responsible for its volatility were more thermodynamically stable at lower temperatures and/or had higher melting and boiling points, relative to the complexes responsible for platinum volatility. No conclusions could be drawn as to an exact nature of such complexes, without determinations of elemental composition and molecular weights, etc.

II. The Analytical Procedure
The procedure is applicable to the concentration levels suggested in the original literature. However, the ten-fold difference between the relative standard deviations reported by the procedure's developers and those achieved in this study suggest inaccuracy in the previously reported values and/or in the application of the procedure in the study. The high cost of the platinum metals encourages and improves the economics of any feasible recovery system, but the low concentrations of the PGM in catalytic converter materials mean that a lot of the capital and labor costs in a system for the PGM's recovery will be for cheap or worthless by-products. High uncertainties and relative standard deviations cast uncertainty on projected efficiencies at any set of conditions — i.e., in run 1303 (a small oval Pt-bearing catalyst sample) the overall recovery was found to be 95.6%, but with a ± 27.3% uncertainty. 62% recovery of Pt versus 95% recovery could make some difference in profitability for a system.
The linear relationship for Pt-complex absorbance versus concentration over 0.75 to 2.50 p.p.m. was confirmed during project work; the range of 0.10 to 0.70 p.p.m. Pt concentration also resulted in a usable, linear working curve. Relative standard deviations were found to be 12 to 25% for such results or slightly higher than those for 1 to 2 p.p.m. of Pt. There was a non-linearity over the 0.65 to 0.80 p.p.m. concentration range in working curves prepared from Pt wire, reagent \( \text{H}_2\text{Pt(OH)}_6 \) and reagent \( \text{H}_2\text{PtCl}_6 \). No mention of this was found in previous literature studied for the project.

Over the 0 to 1.00 p.p.m. range for Pd concentration, the relative standard deviations were lower than those for Pt concentration of similar value. The experimenter feels that the heating involved in the color-development procedure for the determination induces this uncertainty. A communication from Dr. E. L. Kothny of California in June 1978 (after completion of all determinations) suggested that the adopted procedure is consistently low in reported values for Pt concen-
tration whenever Pd is present, and also stated that a combination of his procedure for Pt, plus a separate use of the NDA reagent in determining Pd, would be more reliable and accurate.

III. Application of this System

The Cl₂ plus CO gas-phase treatment approach to platinum metals removal will require further refinement of reactor design and research on optimum conditions to promote volatility of its products prior to a demonstration-level application to industrial use. The Cl₂/NO pair will be more difficult, due to NO's greater costs. Effluent Cl₂ and CO from one reactor can be recycled, converted to innocuous by-products by currently available technology used for pollution control in a number of industries, or perhaps separated, with the CO directed to use as a reducing agent elsewhere in a platinum metals processing plant.

Next to O₂, Cl₂ is industry's least expensive oxidizing gas. It can be produced on-site by small-
to medium-sized electrolytic units or transported into a plant, according to economics.

Certainly, the secondary reclamation of the platinum metals is becoming a serious consideration for the U.S., with fewer primary sources and constantly rising prices. Recycling of the catalytic converter units will likely be mandated by federal authority if not by demands of private industry.
## TABLE I. EXPERIMENTAL RUNS, FEATURING PLUG FLOW OF REACTANT GASES THROUGH SMALL OVAL CHRYSLER CATALYST SAMPLES

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<th>Run #</th>
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<th>Gas Flows in $10^{-6}$ m/s</th>
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**NOTE:** Run numbers relate to the 1977-1978 dates upon which they were performed, e.g., "1007" on 10/7/77, "1324" on 1/24/78.

Heating of the downstream end of the reactor tube was performed with Runs 1111 through 1327. Temperatures of 300-360°C were maintained by means of a heating tape.
## APPENDIX A

### TABLE II. EXPERIMENTAL RUNS, FEATURING PLUG FLOW OF REACTANT GASES THROUGH LARGE OVAL CHRYSLER AND FORD CATALYST SAMPLES

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</tr>
<tr>
<td>1306</td>
<td>4.00</td>
<td>900</td>
<td>4</td>
<td>2.13</td>
<td>0.70</td>
<td>3.50</td>
</tr>
<tr>
<td>1310</td>
<td>4.00</td>
<td>800</td>
<td>6</td>
<td>2.13</td>
<td>0.70</td>
<td>3.50</td>
</tr>
<tr>
<td>1313</td>
<td>4.00</td>
<td>800</td>
<td>2</td>
<td>2.13</td>
<td>0.70</td>
<td>3.50</td>
</tr>
<tr>
<td>1315</td>
<td>4.00</td>
<td>600</td>
<td>6</td>
<td>2.13</td>
<td>0.70</td>
<td>3.50</td>
</tr>
<tr>
<td>1317</td>
<td>4.00</td>
<td>800</td>
<td>2</td>
<td>2.13</td>
<td>0.70</td>
<td>3.50</td>
</tr>
</tbody>
</table>

Using Ford catalyst samples:

<table>
<thead>
<tr>
<th>Sample Run #</th>
<th>Size (grams)</th>
<th>Temp. (°C)</th>
<th>Time (measured in cc/s)</th>
<th>Gas Flows in 10&lt;sup&gt;-6&lt;/sup&gt; m/s</th>
<th>V Ratio</th>
<th>(\text{Cl}_2/\text{CO})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1129</td>
<td>5.00</td>
<td>850</td>
<td>6</td>
<td>2.24</td>
<td>1.33</td>
<td>5.54</td>
</tr>
<tr>
<td>1331</td>
<td>5.00</td>
<td>850</td>
<td>6</td>
<td>2.03</td>
<td>0.70</td>
<td>3.50</td>
</tr>
</tbody>
</table>

* These values represent a flow rate for nitric oxide (NO), used in place of carbon monoxide (CO).

** These values represent the volume to volume ratio for the use of chlorine and nitric oxide gases.

**NOTE:** The downstream end of the reactor tube was heated to 230-400°C during all the above runs, with the exception of Runs 1014 and 1021.
### TABLE III. YIELDS OF PLATINUM CONTENT FROM TREATMENT OF THE SMALL OVAL CHRYSLER CATALYST

<table>
<thead>
<tr>
<th>Run #</th>
<th>Temp. (°C)</th>
<th>Pt Found* in Rinse (%)</th>
<th>Pt Found* in Total (%)</th>
<th>Pt in Rinse relative to Total (ratio • 100%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1007</td>
<td>358</td>
<td>0.44 (±0.02)</td>
<td>74.5 (±7.8)</td>
<td>0.6</td>
</tr>
<tr>
<td>1010</td>
<td>450</td>
<td>3.20 (±0.70)</td>
<td>54.4 (±12.7)</td>
<td>5.9</td>
</tr>
<tr>
<td>1016</td>
<td>600</td>
<td>8.2 (±2.5)</td>
<td>36.7 (±9.4)</td>
<td>22.3</td>
</tr>
<tr>
<td>1017</td>
<td>700</td>
<td>8.04 (±1.90)</td>
<td>40.2 (±9.9)</td>
<td>20.0</td>
</tr>
<tr>
<td>1018</td>
<td>800</td>
<td>30.8 (±8.4)</td>
<td>66.8 (±17.5)</td>
<td>46.1</td>
</tr>
<tr>
<td>1019</td>
<td>910</td>
<td>44.9 (±12.6)</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1024</td>
<td>900</td>
<td>54.7 (±13.6)</td>
<td>73.7 (±18.6)</td>
<td>74.2</td>
</tr>
<tr>
<td>1025</td>
<td>900</td>
<td>69.9 (±10.2)</td>
<td>84.8 (±14.1)</td>
<td>82.4</td>
</tr>
<tr>
<td>1026</td>
<td>1025</td>
<td>38.9 (±10.0)</td>
<td>64.8 (±15.1)</td>
<td>60.0</td>
</tr>
<tr>
<td>1031</td>
<td>450</td>
<td>7.12 (±1.84)</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1050</td>
<td>450</td>
<td>1.96 (±0.64)</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1101</td>
<td>600</td>
<td>3.51 (±1.11)</td>
<td>21.1 (±6.9)</td>
<td>16.6</td>
</tr>
<tr>
<td>1111</td>
<td>350</td>
<td>1.85 (±0.60)</td>
<td>62.6 (±18.0)</td>
<td>2.9</td>
</tr>
<tr>
<td>1115</td>
<td>700</td>
<td>5.58 (±1.38)</td>
<td>26.6 (±7.7)</td>
<td>20.2</td>
</tr>
<tr>
<td>1118</td>
<td>900</td>
<td>25.1 (±9.2)</td>
<td>49.3 (±15.7)</td>
<td>50.5</td>
</tr>
<tr>
<td>1202</td>
<td>900</td>
<td>14.6 (±4.0)</td>
<td>51.2 (±14.1)</td>
<td>23.5</td>
</tr>
<tr>
<td>1216</td>
<td>1025</td>
<td>35.7 (±19.9)</td>
<td>45.4 (±12.6)</td>
<td>79.0</td>
</tr>
<tr>
<td>1305</td>
<td>900</td>
<td>62.2 (±13.5)</td>
<td>95.6 (±27.3)</td>
<td>65.1</td>
</tr>
<tr>
<td>1324</td>
<td>700</td>
<td>8.01 (±2.15)</td>
<td>24.2 (±6.4)</td>
<td>33.1</td>
</tr>
<tr>
<td>1327</td>
<td>700</td>
<td>11.5 (±5.6)</td>
<td>58.0 (±16.4)</td>
<td>19.8</td>
</tr>
</tbody>
</table>

* Percentages of Found Pt refer to the percentage of the Pt content amenable to chemical attack within sample (specimen) determined in the portion. Total Found Pt is a summation of the determinations of Rinse(s) and Residue from a sample.
APPENDIX A

TABLE IV. YIELDS OF PLATINUM AND PALLADIUM CONTENT FROM TREATMENT OF THE LARGE OVAL CHRYSLER AND FORD CATALYSTS

<table>
<thead>
<tr>
<th>Run #</th>
<th>Temp. (°C)</th>
<th>Pt Found in Rinse (%)</th>
<th>Pd Found in Rinse (%)</th>
<th>Pt Found in Total (%)</th>
<th>Pd Found in Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1014</td>
<td>600</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1021</td>
<td>800</td>
<td>18.1(±4.8)</td>
<td>9.3(±2.7)</td>
<td>44.7(±13.3)</td>
<td>110.1(±13.3)</td>
</tr>
<tr>
<td>1047</td>
<td>475</td>
<td>1.72(±0.56)</td>
<td>2.35(±0.58)</td>
<td>78.7(±23.5)</td>
<td>77.4(±16.2)</td>
</tr>
<tr>
<td>1108</td>
<td>600</td>
<td>6.13(±1.75)</td>
<td>7.61(±1.31)</td>
<td>93.1(±23.4)</td>
<td>82.6(±15.2)</td>
</tr>
<tr>
<td>1213</td>
<td>500</td>
<td>3.31(±1.18)</td>
<td>2.66(±0.40)</td>
<td>84.3(±22.1)</td>
<td>90.7(±17.4)</td>
</tr>
<tr>
<td>1120</td>
<td>900</td>
<td>1.5(±0.6)</td>
<td>2.3(±0.3)</td>
<td>10.1(±2.0)</td>
<td>76.3(±10.6)</td>
</tr>
<tr>
<td>1122</td>
<td>450</td>
<td>1.20(±0.32)</td>
<td>3.52(±0.57)</td>
<td>32.4(±8.5)</td>
<td>46.4(±7.6)</td>
</tr>
<tr>
<td>1128</td>
<td>900</td>
<td>9.3(±2.2)</td>
<td>4.74(±0.0)</td>
<td>21.5(±5.7)</td>
<td>66.6(±7.4)</td>
</tr>
<tr>
<td>1206*</td>
<td>700</td>
<td>5.00(±1.37)</td>
<td>4.74(±1.01)</td>
<td>104.1(±25.4)</td>
<td>108.4(-17.0)</td>
</tr>
<tr>
<td>1207*</td>
<td>900</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1211*</td>
<td>900</td>
<td>45.6(±10.7)</td>
<td>8.23(±1.38)</td>
<td>72.5(±18.0)</td>
<td>72.6(±12.3)</td>
</tr>
<tr>
<td>1217*</td>
<td>900</td>
<td>14.4(±1.8)</td>
<td>26.7(±4.6)</td>
<td>35.9(±7.4)</td>
<td>81.3(±12.9)</td>
</tr>
<tr>
<td>1218</td>
<td>1025</td>
<td>50.9(±13.9)</td>
<td>3.93(±0.72)</td>
<td>65.3(±18.2)</td>
<td>62.5(±8.9)</td>
</tr>
<tr>
<td>1306</td>
<td>900</td>
<td>4.3(±1.2)</td>
<td>3.4(±0.9)</td>
<td>29.6(±8.4)</td>
<td>63.0(±9.7)</td>
</tr>
<tr>
<td>1310</td>
<td>800</td>
<td>13.2(±3.0)</td>
<td>20.4(±2.9)</td>
<td>45.4(±10.9)</td>
<td>86.7(±11.8)</td>
</tr>
<tr>
<td>1315</td>
<td>800</td>
<td>10.4(±2.6)</td>
<td>3.54(±0.64)</td>
<td>29.9(±8.0)</td>
<td>54.0(±7.8)</td>
</tr>
<tr>
<td>1316</td>
<td>600</td>
<td>2.9(±1.2)</td>
<td>3.4(±0.6)</td>
<td>73.9(±20.6)</td>
<td>68.5(±7.6)</td>
</tr>
<tr>
<td>1317</td>
<td>800</td>
<td>23.7(±5.9)</td>
<td>15.6(±2.4)</td>
<td>50.5(±12.1)</td>
<td>50.8(±8.4)</td>
</tr>
</tbody>
</table>

* These runs involved use of the Cl₂ plus NO reactant gases system. All others involved use of Cl₂/CO₂ or Cl₂ alone.
APPENDIX B

TABLE V. DISTRIBUTION OF SUBLIMED YIELDS FROM TREATMENT OF THE SMALL OVAL CHRYSLER CATALYST

For Type III Runs¹:

<table>
<thead>
<tr>
<th>Run #</th>
<th>Temp. (°C)</th>
<th>Time (H)</th>
<th>Heat Tape Used?</th>
<th>Heat Amenable Pt Tube Rinse (%)</th>
<th>Amenable Pt Adapt/Trap Rinse (%)</th>
<th>Ratio² Yields</th>
</tr>
</thead>
<tbody>
<tr>
<td>1031</td>
<td>450</td>
<td>4</td>
<td>No</td>
<td>6.77</td>
<td>0.35</td>
<td>19.3</td>
</tr>
<tr>
<td>1115</td>
<td>700</td>
<td>4</td>
<td>Yes</td>
<td>3.98</td>
<td>1.40</td>
<td>2.8</td>
</tr>
<tr>
<td>1118</td>
<td>900</td>
<td>4</td>
<td>Yes</td>
<td>24.6</td>
<td>0.49</td>
<td>50.2</td>
</tr>
<tr>
<td>1202</td>
<td>900</td>
<td>4</td>
<td>Yes</td>
<td>12.7</td>
<td>1.90</td>
<td>6.7</td>
</tr>
<tr>
<td>1019</td>
<td>900</td>
<td>4</td>
<td>No</td>
<td>44.9</td>
<td>7.92</td>
<td>5.7</td>
</tr>
<tr>
<td>1024</td>
<td>900</td>
<td>4</td>
<td>No</td>
<td>3.82</td>
<td>53.2</td>
<td>0.1</td>
</tr>
<tr>
<td>1025</td>
<td>900</td>
<td>6</td>
<td>No</td>
<td>68.2</td>
<td>1.72</td>
<td>39.7</td>
</tr>
<tr>
<td>1303</td>
<td>900</td>
<td>4</td>
<td>Yes</td>
<td>59.1</td>
<td>3.16</td>
<td>18.7</td>
</tr>
<tr>
<td>1216</td>
<td>1025</td>
<td>2</td>
<td>Yes</td>
<td>25.1</td>
<td>10.6</td>
<td>2.4</td>
</tr>
<tr>
<td>1026</td>
<td>1025</td>
<td>4</td>
<td>No</td>
<td>25.9</td>
<td>13.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

ALL RUNS EXCEPT 1118 (no CO added) and 1303 (a 3.04 ratio) WERE CONDUCTED WITH A Cl₂/CO VOLUME FLOW RATIO OF 1.68.

¹Type I Collection: For the sample, Rinse of the Reactor Tube, Adapter, and Trap were collected and analyzed independently, following the run.

Type II Collection: Rinse of the Tube and Adapter were collected and analyzed together, with the Trap Rinse processed separately.

Type III Collection: The Tube Rinse and Adapter+Trap Rinse were collected and analyzed independently.

Type IV Collection: All Rinse factions were analyzed together.

From runs involving samples from gas-phase treatment of the small oval Chrysler S/C, no Type I collections were made; Runs 1324 & 1327 were collected in the Type II manner; Runs 1007, 1010, 1011, 1016 & 1017 were collected in the Type IV manner; all others were collected as per Type III.

²"Ratio Yields" denotes the quotient of the percentage of sample's amenable Pt in the Tube Rinse divided by the percentage of sample's amenable Pt in the Adapter plus Trap Rinse.
## APPENDIX B

### TABLE VI. DISTRIBUTION OF SUBLIMED YIELDS FROM TREATMENT OF THE LARGE OVAL CHRYSLER CATALYST

**PART 1. Type II Run Results.**

<table>
<thead>
<tr>
<th>Run #</th>
<th>Temp. (°C)</th>
<th>Time (H)</th>
<th>Cl₂/CO Ratio (V/V)</th>
<th>Amenable Pt/Pd Ratio (V/V)</th>
<th>Tube/Adapt Rinse (%)</th>
<th>Trap Rinse (%)</th>
<th>Ratio³</th>
<th>Yields Pt</th>
<th>Yields Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1315</td>
<td>600</td>
<td>6</td>
<td>3.04</td>
<td>2.68/2.60</td>
<td>0.21/0.78</td>
<td>12.8</td>
<td>3.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1317</td>
<td>800</td>
<td>2</td>
<td>1.69</td>
<td>21.8/11.7</td>
<td>1.96/3.90</td>
<td>11.1</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1313</td>
<td>800</td>
<td>4</td>
<td>3.04</td>
<td>9.49/3.39</td>
<td>0.87/0.15</td>
<td>10.9</td>
<td>22.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1310</td>
<td>800</td>
<td>6</td>
<td>3.04</td>
<td>12.9/12.9</td>
<td>0.28/7.55</td>
<td>46.1</td>
<td>1.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹Types of collection patterns are described with Table V. Runs collected in the Type III pattern are listed in Part 2 of this Table. Runs 1120, 1122 & 1306 were collected in the Type I pattern, with no samples involving samples of the large oval Chrysler S/C collected in the Type IV manner.

²"Ratio Yield" denotes the quotient of the percentage of sample's amenable Pt (or Pd) in the Tube/Adapter Rinse divided by the percentage of amenable Pt (or Pd) in the Trap Rinse.
APPENDIX B

TABLE VI. DISTRIBUTION OF SUBLIMED YIELDS FROM TREATMENT OF THE LARGE OVAL CHRYSLER CATALYST

PART 2. Type III Run Results

<table>
<thead>
<tr>
<th>Run #</th>
<th>Tmp. (°C)</th>
<th>Time (H)</th>
<th>Cl₂/CO Ratio (V/V)</th>
<th>Amenable Pt/Pd Tube Rinse (%)</th>
<th>Amenable Pt/Pd Adapt/Trap Rinse (%)</th>
<th>Ratio Yields¹</th>
<th>Pt</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1113</td>
<td>350</td>
<td>4</td>
<td>1.68</td>
<td>1.79/ 2.50</td>
<td>1.52/ 0.16</td>
<td>1.2</td>
<td>15.6</td>
<td></td>
</tr>
<tr>
<td>1104</td>
<td>475</td>
<td>4</td>
<td>1.68</td>
<td>1.47/ 2.35</td>
<td>0.21/ 0</td>
<td>5.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1108</td>
<td>600</td>
<td>4</td>
<td>1.68</td>
<td>4.00/ 1.98</td>
<td>2.13/ 5.63</td>
<td>1.88</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>1021</td>
<td>800</td>
<td>4½</td>
<td>1.68</td>
<td>10.2/13.8</td>
<td>7.86/ 5.51</td>
<td>1.30</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>1128</td>
<td>900</td>
<td>4</td>
<td>1.68</td>
<td>8.84/ 2.17</td>
<td>0.51/ 1.06</td>
<td>17.3</td>
<td>2.05</td>
<td></td>
</tr>
<tr>
<td>1218</td>
<td>1025</td>
<td>4</td>
<td>1.69</td>
<td>45.5/ 2.08</td>
<td>5.36/ 1.85</td>
<td>8.49</td>
<td>1.12</td>
<td></td>
</tr>
</tbody>
</table>

¹"Ratio Yields" denotes the quotient of the percentage of amenable Pt (or Pd) in the Tube Rinse divided by the percentage of amenable Pt(or Pd) in the Adapter/ Trap Rinse.
APPENDIX C

CALCULATION OF METAL CONCENTRATION VALUES FROM COLORIMETRIC DETERMINATION OF PT AND PD

The following represents a summary of the calculations of values for a run's analytical results; values for Pt content from run 1018 (a Pt-only sample) have been selected for an example. "Residue" refers to the solution of metal(s) dissolved from the chemically-attacked S/C sample following a gas-phase run or equivalent liquid-phase attack procedure using aqua regia. "Rinse," or "Tube Rinse," etc. refers to a solution which has resulted from the collection of PGM-bearing sublimates from the inside walls of the reaction glassware following a run. Sequentially, each result was processed as follows:

1. The average of the absorbance values from the 3 to 6 aliquots color developed is calculated. This averaged result represents the absorbance due to Pt plus Pt complexes in solution. For example, the net average of 4 color developed aliquots' absorbances - 0.220, .215, .220 and .211 was 0.217.
2. Any absorbance value at 525 nanometers for the non-color developed aliquots is due to Pd or other ions complexed w/NDA. Such a value is usually zero for the Pt-only catalyst. For run 1018's 3 non-color developed aliquots, there was no absorbance; hence a conclusion of no Fe or Pd content was made.

3. The value for absorbance due to total Pt + Pd (or Pt) is co-ordinated with the corresponding concentration for the Pt-NDA complex known to give such a value for "absorbance." This is done on a previously plotted graph of A versus Pt concentration. Parallel maxima and minima for each point on the curve allow determination of error for a determined value of Pt.

For example, A of 0.217 corresponded to 0.94 (±.12) p.p.m. Pt.

4. Grams Pt in the sample are then determined by the relationship formula:

\[
\text{Grams Pt} = \frac{\text{Concentration (in p.p.m.)} \cdot 10^{-3} \cdot (\text{"Dilution factor"}) \cdot (\text{volume of sample in mL/dvided by 1000 mL})}{\text{(volume of sample in mL/divided by 1000 mL)}}
\]

Where "Dilution factor" refers to the quotient of the original sample ("master") volume divided by the accurate volume of that sample in the aliquot used for Pt determination. Such dilution factors may range from 1 to 100 or more.

For run 1018's residue sample,

\[
\text{Grams Pt} = (0.94 \pm 0.12) \cdot 10^{-3} \cdot \frac{50}{2} \cdot \frac{50\text{mL}}{1000\text{mL}}, \text{ or,}
\]
1.18 (±0.15) x 10^{-3} grams Pt in the sample.

5. At this point, the determined values of Pt (and Pd) per gram S/C sample are multiplied against the original sample weight used in the run.

In this example,

1.14 (±0.15) x 10^{-3} grams Pt • 3.00 grams sample per gram S/C

gave 3.42 (±0.45) x 10^{-3} grams Pt present.

6. Where more than one set of aliquots have been developed for a sample, such as 2 sets, each on a separate lab date, the values for each date's sample can be combined and average, for a more accurate value. For example, a later date's analysis of the run 1018 residue sample yielded a value of 1.28 (±0.15) x 10^{-3} grams Pt. An average of this value and that from the first determination would be 1.23 (±0.15) x 10^{-3} gram Pt.

7. The percentage of the total available Pt obtained by the run (chemically attacked) is calculated by this relationship:

\[
\% \text{ available Pt} = \frac{\text{Value for Pt obtained (grams)}}{\text{value for available Pt (grams)}} \times 100\%
\]

For example, for run 1018,

\[
1.23(±.15) \times 10^{-3} \text{ grams} \times 100\% = 36.0(±9.14)\%
\]

3.42(±.42) x 10^{-3} grams

Platinum in the various rinse samples resulting from the run could be calculated, and a total compared to the total available Pt in the
original sample.

8. Palladium must be calculated wherever evidenced in the non-color developed aliquots for a sample; the values for absorbance due to Pd are subtracted from those for Pt prior to calculation of Pt concentration, as in step 3.

9. The uncertainty % given in step is derived by a calculation based on the absolute uncertainties for each value, e.g., a relation of \( p(\text{uncertainty}) = \text{result} \% \cdot \left( \frac{a}{A} + \frac{b}{B} \right) \).

(Where A and B are the dividend and divisor values, and a and b are their respective uncertainties.)

For example for the 1018 "residue,"

\[
\begin{align*}
A &= 1.23 \times 10^{-3} \text{ g Pt} \quad \text{and} \quad a = \pm 1.15 \times 10^{-3} \text{ g Pt} \\
B &= 3.42 \times 10^{-3} \text{ g Pt} \quad \text{and} \quad b = \pm 4.45 \times 10^{-3} \text{ g Pt} \\
p &= 36.0 \cdot \left( \frac{1.15}{1.23} + \frac{4.45}{3.42} \right) = 9.14(\%) 
\end{align*}
\]
### APPENDIX D

#### TABLE VII. YIELDS OF PLATINUM RELATIVE TO TEMPERATURE FOR THE SMALL OVAL CATALYST

<table>
<thead>
<tr>
<th>Run #</th>
<th>Temp. (°C)</th>
<th>Amenable Pt in Residue (%)</th>
<th>Amenable Pt in Rinses (%)</th>
<th>Pt Yield Overall (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1111</td>
<td>350</td>
<td>60.8 (±17.4)</td>
<td>1.83 (±0.60)</td>
<td>62.6 (±18.0)</td>
</tr>
<tr>
<td>1010</td>
<td>450</td>
<td>51.2 (±12.0)</td>
<td>3.20 (±0.70)</td>
<td>54.4 (±12.7)</td>
</tr>
<tr>
<td>1115*</td>
<td>700</td>
<td>21.2 (±6.3)</td>
<td>5.38 (±1.38)</td>
<td>26.6 (±7.7)</td>
</tr>
<tr>
<td>1017*</td>
<td>700</td>
<td>32.2 (±8.0)</td>
<td>8.04 (±1.90)</td>
<td>40.2 (±9.9)</td>
</tr>
<tr>
<td>1018</td>
<td>800</td>
<td>36.0 (±9.1)</td>
<td>30.8 (±8.4)</td>
<td>66.8 (±17.5)</td>
</tr>
<tr>
<td>1024</td>
<td>900</td>
<td>19.0 (±5.0)</td>
<td>54.7 (±13.6)</td>
<td>73.7 (±18.6)</td>
</tr>
<tr>
<td>1026</td>
<td>1025</td>
<td>9.12 (±3.1)</td>
<td>36.9 (±10.0)</td>
<td>44.8 (±13.1)</td>
</tr>
<tr>
<td>*Average of Runs</td>
<td></td>
<td></td>
<td></td>
<td>26.7</td>
</tr>
</tbody>
</table>

**ALL RUNS WERE OVER 4 HOURS OF REACTANT GAS FLOW, AT THE Cl₂/CO (V/V) RATIO OF 1.68 (±0.02).**

#### TABLE VIII. YIELDS OF PLATINUM RELATIVE TO CO CONTENT IN A Cl₂ PLUS CO MIXTURE OF REACTANT GASES

<table>
<thead>
<tr>
<th>Run #</th>
<th>Ratio Cl₂/CO (V/V)</th>
<th>Chlorine in Flow (%)</th>
<th>Amenable Pt in Rinses (%)</th>
<th>Amenable Pt in Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1118</td>
<td>1.00</td>
<td>100</td>
<td>25.1 (±9.2)</td>
<td>49.3 (±15.7)</td>
</tr>
<tr>
<td>1202</td>
<td>5.60</td>
<td>85</td>
<td>14.6 (±4.0)</td>
<td>51.2 (±14.1)</td>
</tr>
<tr>
<td>1503</td>
<td>3.04</td>
<td>75</td>
<td>62.2 (±13.6)</td>
<td>95.6 (±27.3)</td>
</tr>
<tr>
<td>1024</td>
<td>1.68</td>
<td>63</td>
<td>54.7 (±13.6)</td>
<td>73.7 (±18.6)</td>
</tr>
</tbody>
</table>

**ALL RUNS WERE CONDUCTED OVER 4 HOURS REACTANT GAS FLOW AT 900°C, WITH SAMPLES OF THE SMALL OVAL CHRYSLER S/C**

1 No CO flowed during Run 1118.
FIGURE 2.1 YIELDS OF PLATINUM AS A FUNCTION OF TEMPERATURE, USING Cl₂/CO TREATMENT OF THE SMALL OVAL CHRYSLER CATALYST

Legend
- = Rinse Yield for Pt
- = Total Yield for Pt from Run's determinations
Y-axis--Each increment represents 1% of amenable Pt in sample
X-axis--Each increment represents 12.5°C (over 350-1050°C)
**APPENDIX E**

**TABLE IX. YIELDS OF PLATINUM AND PALLADIUM AS A FUNCTION OF TEMPERATURE IN THE TREATMENT OF THE LARGE OVAL TYPE CATALYST**

<table>
<thead>
<tr>
<th>Run #</th>
<th>Temp. (°C)</th>
<th>Amenable Pt in Rinses (%)</th>
<th>Amenable Pd in Rinses (%)</th>
<th>Amenable Pt in Total (%)</th>
<th>Amenable Pd in Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1113</td>
<td>350</td>
<td>3.31 (+ 1.18)</td>
<td>2.66 (+ 0.40)</td>
<td>84.3 (+ 22.1)</td>
<td>90.7 (+ 17.4)</td>
</tr>
<tr>
<td>1104</td>
<td>450</td>
<td>1.72 (+ 0.56)</td>
<td>2.35 (+ 0.58)</td>
<td>78.7 (+ 25.2)</td>
<td>77.4 (+ 16.2)</td>
</tr>
<tr>
<td>1108</td>
<td>600</td>
<td>6.13 (+ 1.75)</td>
<td>7.61 (+ 1.31)</td>
<td>93.1 (+ 23.4)</td>
<td>82.6 (+ 15.2)</td>
</tr>
<tr>
<td>1021</td>
<td>800</td>
<td>18.1 (+ 4.8)</td>
<td>19.3 (+ 2.7)</td>
<td>44.7 (+ 13.3)</td>
<td>110.1 (+ 13.6)</td>
</tr>
<tr>
<td>1128</td>
<td>900</td>
<td>9.3 (+ 2.2)</td>
<td>3.3 (+ 0.6)</td>
<td>21.5 (+ 5.7)</td>
<td>66.6 (+ 7.4)</td>
</tr>
<tr>
<td>1218</td>
<td>1025</td>
<td>50.9 (+ 13.9)</td>
<td>3.93 (+ 0.72)</td>
<td>65.5 (+ 18.2)</td>
<td>62.5 (+ 8.9)</td>
</tr>
</tbody>
</table>

All runs were conducted at a reactant gas flow ratio of 1.69 (Cl₂/CO) over 4 hours.
FIGURE 3.1

YIELDS OF PLATINUM AND PALLADIUM AS A FUNCTION OF TEMPERATURE, USING Cl₂/CO TREATMENT OF THE LARGE OVAL CATALYST

LEGEND
- Rinse Yield for Pt
× Rinse Yield for Pd
○ Total Run’s Yield for Pt
□ Total Run’s Yield for Pd

Y-axis—Each increment is 1.5% of amenable Pt (or Pd) for sample
X-axis—Each increment is 12.5° Celsius (of reaction temp.)
## APPENDIX E

### TABLE X. YIELDS OF PLATINUM AND PALLADIUM AS A FUNCTION OF THE REACTANT GASES CONCENTRATIONS

<table>
<thead>
<tr>
<th>Run #</th>
<th>Cl₂/CO Ratio (V/V)</th>
<th>Amenable Pt in Rinses (%)</th>
<th>Amenable Pd in Rinses (%)</th>
<th>Amenable Pt in Total* (%)</th>
<th>Amenable Pd in Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1108</td>
<td>1.68</td>
<td>6.1 (+ 1.8)</td>
<td>7.6 (+ 1.3)</td>
<td>93.2 (+ 23.4)</td>
<td>32.6 (+ 15.2)</td>
</tr>
<tr>
<td>1315</td>
<td>3.04</td>
<td>2.9 (- 1.2)</td>
<td>3.4 (- 0.6)</td>
<td>73.9 (- 20.0)</td>
<td>68.5 (- 7.6)</td>
</tr>
<tr>
<td>1128</td>
<td>1.68</td>
<td>9.3 (+ 2.2)</td>
<td>3.3 (+ 0.6)</td>
<td>21.5 (+ 5.7)</td>
<td>66.6 (+ 7.4)</td>
</tr>
<tr>
<td>1306</td>
<td>3.04</td>
<td>4.3 (- 1.2)</td>
<td>3.4 (+ 0.9)</td>
<td>29.6 (- 8.4)</td>
<td>63.0 (- 9.7)</td>
</tr>
<tr>
<td>1317</td>
<td>1.68</td>
<td>23.7 (+ 5.9)</td>
<td>15.6 (+ 2.4)</td>
<td>50.5 (+ 12.1)</td>
<td>50.8 (+ 8.4)</td>
</tr>
<tr>
<td>1313</td>
<td>3.04</td>
<td>10.4 (- 2.6)</td>
<td>3.5 (- 0.6)</td>
<td>29.9 (- 8.0)</td>
<td>54.0 (- 7.8)</td>
</tr>
<tr>
<td>1129</td>
<td>1.68</td>
<td>41.3 (+ 15.7)</td>
<td>76.7 (+ 9.8)</td>
<td>43.3 (+ 16.4)</td>
<td>79.0 (+ 10.1)</td>
</tr>
<tr>
<td>1331</td>
<td>3.04</td>
<td>91.3 (- 31.8)</td>
<td>60.4 (- 6.3)</td>
<td>13.4 (- 32.3)</td>
<td>61.6 (- 6.4)</td>
</tr>
</tbody>
</table>

* Total refers to the value for total metal content of the sample, usually the sum of independent values for the 2 or more Rinse fractions and the Residue fraction, and compared to the figure for amenable Pt or Pd from an amount of sample of that run's size.
### APPENDIX E

#### TABLE XI. YIELDS OF PLATINUM AND PALLADIUM AS A FUNCTION OF TIME FOR REACTANT GAS FLOW

<table>
<thead>
<tr>
<th>RUN #</th>
<th>Temp. (°C)</th>
<th>Cl₂/CO Ratio</th>
<th>Time (h)</th>
<th>Percentage of Metal Relative to Actual Content in Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>% Platinum In Rinse</td>
</tr>
<tr>
<td>1104</td>
<td>450</td>
<td>1.68</td>
<td>4</td>
<td>1.72 (±0.56) 78.7 (±23.5)</td>
</tr>
<tr>
<td>1122</td>
<td>450</td>
<td>1.68</td>
<td>6</td>
<td>1.20 (±0.32) 32.4 (±8.5)</td>
</tr>
<tr>
<td>1317</td>
<td>800</td>
<td>1.68</td>
<td>2</td>
<td>23.7 (±6.0) 50.6 (±12.2)</td>
</tr>
<tr>
<td>1021</td>
<td>800</td>
<td>1.68</td>
<td>4</td>
<td>18.1 (±4.8) 44.7 (±13.3)</td>
</tr>
<tr>
<td>1128</td>
<td>900</td>
<td>1.68</td>
<td>4</td>
<td>9.35 (±2.18) 21.6 (±5.7)</td>
</tr>
<tr>
<td>1120</td>
<td>900</td>
<td>1.68</td>
<td>6</td>
<td>1.5 (±0.6) 10.1 (±2.0)</td>
</tr>
<tr>
<td>1313</td>
<td>800</td>
<td>3.04</td>
<td>2</td>
<td>10.4 (±2.60) 29.9 (±8.0)</td>
</tr>
<tr>
<td>1310</td>
<td>800</td>
<td>3.04</td>
<td>6</td>
<td>13.2 (±3.00) 45.4 (±10.9)</td>
</tr>
</tbody>
</table>

SAMPLES WERE ALL OF THE LARGE OVAL CHRYSLER CATALYST.

**COMMENT:** Of these four sets, in only one case does an increase of time bring about a uniform increase of yields for both metals—in Runs 1313 and 1310, the higher chlorine content results in major increases in sublimed Pt and Pd, as well as in the overall level of chemical attack throughout the sample.
<table>
<thead>
<tr>
<th>Run #</th>
<th>Ttemp. (°C)</th>
<th>Amenable Pt/Pd</th>
<th>Amenable Pt/Pd</th>
<th>Total Pt/Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>In Residue (%)</td>
<td>In Rinses (%)</td>
<td>In Sample (%)</td>
</tr>
<tr>
<td>1206</td>
<td>700</td>
<td>99.1/103.7</td>
<td>5.00/4.74</td>
<td>104.1/108.4</td>
</tr>
<tr>
<td>1211</td>
<td>900</td>
<td>26.9/64.6</td>
<td>45.6/8.23</td>
<td>72.5/72.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run #</th>
<th>Ratio Cl₂/NO (V/V)</th>
<th>Amenable Pt/Pd</th>
<th>Amenable Pt/Pd</th>
<th>Total Pt/Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>In Residue (%)</td>
<td>In Rinses (%)</td>
<td>Found (%)</td>
</tr>
<tr>
<td>1212</td>
<td>2.7</td>
<td>21.5/54.6</td>
<td>14.4/26.7</td>
<td>35.9/81.3</td>
</tr>
<tr>
<td>1211</td>
<td>5.2</td>
<td>26.9/64.6</td>
<td>45.6/8.23</td>
<td>72.5/72.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run #</th>
<th>Ratio Cl₂/X (V/V)</th>
<th>Amenable Pt/Pd</th>
<th>Amenable Pt/Pd</th>
<th>Total Pt/Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>In Residue (%)</td>
<td>In Rinses (%)</td>
<td>Found (%)</td>
</tr>
<tr>
<td>1211</td>
<td>Cl₂/NO=5.2</td>
<td>26.9/64.6</td>
<td>45.6/8.23</td>
<td>72.5/72.6</td>
</tr>
<tr>
<td>1306</td>
<td>Cl₂/CO=3.0</td>
<td>25.3/59.6</td>
<td>4.22/3.26</td>
<td>29.5/63.0</td>
</tr>
<tr>
<td>1128</td>
<td>Cl₂/CO=1.7</td>
<td>12.2/63.3</td>
<td>9.35/3.23</td>
<td>21.6/66.5</td>
</tr>
</tbody>
</table>

**ALL THREE RUNS WERE CONDUCTED AT 900°C OVER 4 HOURS**

'These data are presented for comparison of the yields from use of the two gas systems under otherwise identical conditions.'
TABLE XIII. RELATIVE YIELDS OF PLATINUM FROM THE LARGE OVAL CHRYSLER CATALYST AND THE SMALL OVAL CHRYSLER CATALYST UNDER SIMILAR REACTION CONDITIONS

<table>
<thead>
<tr>
<th>Run #</th>
<th>Temp. (°C)</th>
<th>Ratio Cl₂/CO (V/V)</th>
<th>Time (H)</th>
<th>Catalyst Type</th>
<th>Amenable Pt (%)</th>
<th>Total Pt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1026</td>
<td>1025</td>
<td>1.69</td>
<td>4</td>
<td>Small</td>
<td>38.9</td>
<td>48.0</td>
</tr>
<tr>
<td>1218</td>
<td>1025</td>
<td>1.69</td>
<td>4</td>
<td>Large</td>
<td>50.9</td>
<td>65.3</td>
</tr>
<tr>
<td>1111</td>
<td>350</td>
<td>1.69</td>
<td>4</td>
<td>Small</td>
<td>1.8</td>
<td>62.6</td>
</tr>
<tr>
<td>1115</td>
<td>350</td>
<td>1.69</td>
<td>4</td>
<td>Large</td>
<td>3.3</td>
<td>84.3</td>
</tr>
<tr>
<td>1031</td>
<td>450</td>
<td>1.69</td>
<td>4</td>
<td>Small</td>
<td>7.1</td>
<td>100.0+</td>
</tr>
<tr>
<td>1010</td>
<td>450</td>
<td>1.69</td>
<td>4</td>
<td>Small</td>
<td>3.2</td>
<td>54.4</td>
</tr>
<tr>
<td>1104</td>
<td>450</td>
<td>1.69</td>
<td>4</td>
<td>Large</td>
<td>1.7</td>
<td>78.7</td>
</tr>
<tr>
<td>1024</td>
<td>900</td>
<td>1.68</td>
<td>4</td>
<td>Small</td>
<td>54.7</td>
<td>73.7</td>
</tr>
<tr>
<td>1123</td>
<td>900</td>
<td>1.68</td>
<td>4</td>
<td>Large</td>
<td>9.3</td>
<td>21.5</td>
</tr>
<tr>
<td>1303</td>
<td>900</td>
<td>3.04</td>
<td>4</td>
<td>Small</td>
<td>62.2</td>
<td>95.7</td>
</tr>
<tr>
<td>1306</td>
<td>900</td>
<td>3.04</td>
<td>4</td>
<td>Large</td>
<td>4.2</td>
<td>29.6</td>
</tr>
<tr>
<td>1025</td>
<td>900</td>
<td>1.69</td>
<td>6</td>
<td>Small</td>
<td>69.5</td>
<td>84.8</td>
</tr>
<tr>
<td>1120</td>
<td>900</td>
<td>1.69</td>
<td>6</td>
<td>Large</td>
<td>1.5</td>
<td>10.1</td>
</tr>
</tbody>
</table>
LITERATURE CITED


(2) Simmons, Lionel E. Simmons Precious Metals Letter 1978, 11(2), 2.


(15) Haitlis, 1971, p 56.


