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The Indirect Gas Chromatographic Determination of Palladium in an Aqueous Solution

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An indirect method has been proposed for the gas-chromatographic determination of palladium in an aqueous solution. After a mixture of propylene and propane has come in contact with a palladium sample solution, the amount of propylene in the remaining gas is estimated, propane being used as an internal standard. An apparatus consisting of a gas sampler, a gas tank, *etc.* was devised. The reaction between propylene and palladium ions in less than 3.0 N perchloric acid goes to completion within 15 min. According to the present method, the calibration curve is straight for Pd up to 500 ppm and for Hg up to 1500 ppm. The following ions in concentrations less than that of Pd^{2+} are tolerable; Co^{2+}, Mg^{2+}, Mn^{2+}, Li^+, Sn^{4+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Al^{3+}, ClO_4^-, Cl^-, NO_3^-, CH_3COO^-, and SO_4^{2-}, while Fe^{3+}, Ag^+, Hg^{2+}, Pt^{2+} and Pt^{4+} interfere seriously. The interference of ferric, silver, and mercuric ions can be avoided by chloride or bromide precipitation, followed by passing the substances through a cation exchanger column. The behavior of the mercuric ion in the presence of the palladium ion, which is quite different from that of the mercuric ion alone, has also been discussed.

As a typical example of the gas-chromatographic determination of non-volatile substances, the indirect determination of palladium in an aqueous solution has been previously reported by the authors[1] in this journal as a short communication. The present paper will offer the detailed results obtained thereafter by using an improved procedure.

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[1] T. Koga and T. Hara, This Bulletin, **39**, 1353 (1966).

Experimental

Reagents. A stock solution of palladium perchlorate was prepared by dissolving palladium chloride (purity >99.5%) in perchloric acid. The chloride ions were expelled by evaporation. The solution was standardized gravimetrically. All the other chemicals used were of analytical reagent grade.

Apparatus. Commercial propane was purified by passing it through concentrated sulfuric acid. The purified propane was proved to be free from any olefins. Propylene, obtained from the Maruzen Sekiyu Co., was 95.4% pure; although it contained 4.3% propane, the other impurities may be accounted negligible for the present work. Both gases were stored separately in gas holders, as is shown in Fig. 1. This type of apparatus, in which a gas is replaced with water, is not, however, suitable for a mixture of propylene and propane in a definite mole ratio since their solubilities in water are different. In order to introduce propane and propylene into a gas sampler (Fig. 3) under a definite pressure, the gases are at first led into two bottles, A_3 and B_3 respectively, and then driven out of them into a gas sampler through columns of anhydrous calcium chloride.

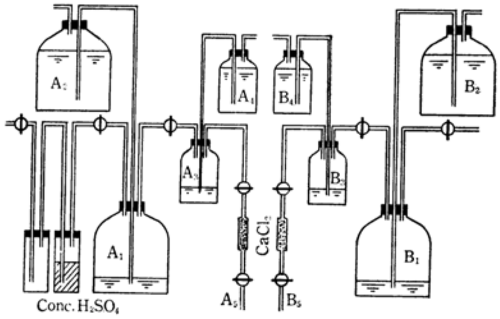

Fig. 1. Gas holders.

A_1, A_3 : Propane gas holders
B_1, B_3 : Propylene gas holders
A_2, A_4, B_2, B_4 : Water tanks
A_5, B_5 : Gas outlets

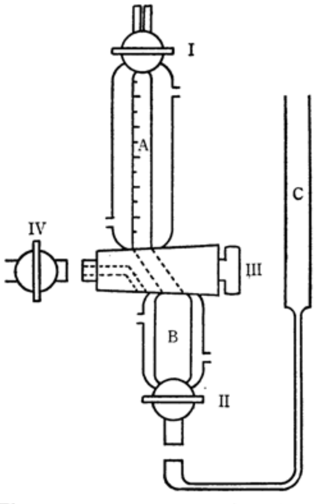

Fig. 2. The apparatus to examine the gas-liquid equilibrium and the reaction between propylene and an aqueous palladium solution.
A : Gas burette, B : Sample bottle, C : Leveler

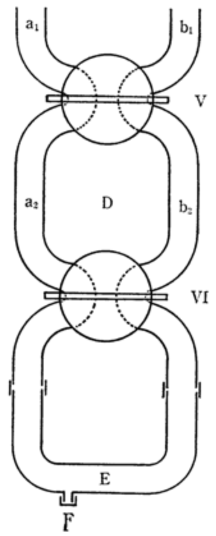

Fig. 3. Gas sampler and U-tube.
D : Gas sample E : U-tube
F : Sample soln. inlet

The apparatus shown in Fig. 2 was devised in order to examine the gas-liquid equilibrium and the reaction between propylene and an aqueous palladium solution. In Fig. 2, (A) is a 20 m*l* gas burette, and (B), a 30 m*l* sample bottle. A sample solution is taken in (C), and the level is brought up to the top of Cock III. (A) is connected with a gas holder through Cocks III and IV, and evacuated through Cock II. After closing Cock II, the gas is brought into (A) from a gas holder. (A), (B), and Cock IV are separated by adjusting Cock III, and internal pressure of (A) is made equal to the atmospheric pressure by rapidly operating Cock II. Cock III is opened, and the gas and sample solution are made to come in contact with each other by turning the apparatus. After a definite time, (C) is filled with a solution the same as the sample solution and Cock I is opened. The water levels in (A) and (C) are balanced rapidly, and the burette is read.

To take in a definite volumes of propane and propylene, the a_1 and b_1 of the gas sampler shown in Fig. 3 are connected with A_5 and B_5 (Fig. 1) respectively, and a_2 (1.0 m*l* capacity) and b_2 (0.5 m*l* capacity) are filled with propane and propylene respectively. Then, the U-tube, E, is connected as shown in Fig. 3, and 5 m*l* of a sample solution is added through the inlet, F; the U-tube is filled with distilled water (about 1.0 m*l*) and stoppered by Silicone rubber. The gas is made to come in contact with the sample solution by opening Cock VI and by turning the apparatus for a definite time in a water bath at 25±0.1°C. The resulting gas is collected in a_2 and b_2; b_1 is charged with anhydrous calcium chloride, and a_1 and b_1 are connected with a Yanagimoto GCG-5DH gas chromatograph. The gas is swept with a carrier gas by turning Cock V and analyzed under the following conditions: carrier gas, He; flow rate, 20 m*l*/min; column, 2 m long, charged with alumina (50—100 mesh and heated at 200—300°C for 2 hr), and coated with 2% liquid paraffin; column temp., 55°C; detector, thermal conductivity type.

Results and Discussion

The Equilibrium between Gas and Liquid Phases. The amounts of propane and propylene absorbed into the distilled water and 1.5 N perchloric acid containing 4800 μg of palladium were measured by the apparatus shown in Fig. 2; they are given in Table 1.

TABLE 1. THE ABSORPTION OF PROPANE AND PROPYLENE INTO AQUEOUS SOLUTIONS AT 25°C

Contact time min	Propane absorbed in H_2O ml	Propylene absorbed		V_2-V_1 ml
		in H_2O ml (V_1)	in Pd^{2+} soln.* ml (V_2)	
5	—	2.30	—	—
10	0.6	2.55	3.55	1.00
15	—	2.60	3.60	1.00
20	0.6	2.60	3.60	1.00
25	—	2.60	—	—
30	0.6	2.60	3.60	1.00

* 4800 μg Pd/1.5 N $HClO_4$

It may be seen from Table 1 that the equilibrium between gas and liquid phases is attained in 10—15 min regardless of whether palladium ions are present or absent. This is concordant with the fact that palladium ions are immediately reduced to the metal when they come in contact with propylene, thus producing a black solution. The dissolution of propylene is, therefore, the rate-determining step for the reaction between propylene and palladium ions. The difference between the

TABLE 2. THE EFFECTS OF THE ACID CONCENTRATION ON THE ABSORPTION OF PROPYLENE AT 25°C

Pd taken: 5745 μg, Contact time: 20 min

$HClO_4$ N	The amounts absorbed in Pd^{2+} soln. ml
1.0	4.20
2.0	4.20
3.0	4.20
4.0	4.05
5.0	4.05
6.0	3.70

TABLE 3. THE EFFECTS OF DIVERSE IONS

Pd^{2+} taken: 800 μg, Acidity: 0.4 N $HClO_4$

Ions	The formulas of salts	The mole ratio Pd : ions	The ratios against a blank	Pd found μg	Relative errors %
Co^{2+}	Chloride	1 : 1	0.821	873	+9.12
Mg^{2+}	Chloride	1 : 1	0.822	868	+8.50
Mn^{2+}	Chloride	1 : 1	0.822	868	+8.50
Li^{+}	Chloride	1 : 1	0.845	756	−5.50
Sn^{4+}	Chloride	1 : 1	0.843	766	−4.25
Ni^{2+}	Perchlorate	1 : 1	0.830	829	+3.62
Cu^{2+}	Perchlorate	1 : 1	0.825	854	+6.75
Cd^{2+}	Perchlorate	1 : 1	0.839	785	−1.88
Zn^{2+}	Perchlorate	1 : 1	0.842	771	−3.62
Pb^{2+}	Nitrate	1 : 1	0.840	780	−2.50
Al^{3+}	Nitrate	1 : 1	0.820	878	+9.75
Hg^{2+}	Perchlorate	1 : 1	0.687	1527	+90.9
Fe^{3+}	Chloride	1 : 1	0.792	1015	+26.9
Ag^{+}	Nitrate	1 : 1	0.747	1234	+54.3
Pt^{2+}	*	1 : 1	0.612	1893	+136
Pt^{4+}	**	1 : 1	0.614	1882	+135
ClO_4^-	Sodium salt	1 : 1	0.833	815	+1.88
Cl^-	Sodium salt	1 : 1	0.837	795	−0.63
Cl^-	Sodium salt	1 : 5	0.825	854	+6.75
Cl^-	Sodium salt	1 : 10	0.832	820	+2.50
NO_3^-	Sodium salt	1 : 1	0.843	766	−4.25
NO_3^-	Sodium salt	1 : 5	0.825	854	+6.75
NO_3^-	Sodium salt	1 : 10	0.828	839	+4.88
CH_3COO^-	Sodium salt	1 : 5	0.831	824	+3.00
CH_3COO^-	Sodium salt	1 : 10	0.831	824	+3.00
SO_4^{2-}	Sodium salt	1 : 5	0.840	780	−2.50
SO_4^{2-}	Sodium salt	1 : 10	0.846	751	−6.13

* Potassium tetrachloroplatinate

** Potassium hexachloroplatinate

amounts of propylene absorbed into the water and the palladium solution is just 1.00 m*l* at 25°C; this agrees with the theoretical amount, 1.10 m*l*, corresponding to 4800 μg Pd^{2+}. It may, therefore, be supposed that the reaction between palladium ions and propylene has gone to completion, since the dissolution of propylene was not affected by the 1.5 N perchloric acid.

The Effect of the Acid Concentration. The amount of propylene absorbed was measured similarly in various concentrations of perchloric acid in the presence of 5745 μg Pd^{2+}. The results are shown in Table 2. No interference was found up to 3 N.

The Calibration Curves. Up to 800 ppm Pd^{2+} was taken into the apparatus (Fig. 3) and allowed to react with a mixture of propane and propylene in 0.4 N perchloric acid in accordance with the above-mentioned procedure; we next made a gas chromatographic determination of the resulting gas. The calibration curve for palladium was obtained by plotting the concentration of palladium as the abscissa and the value of $\{A_{py}/A_{pa}\}_2/\{A_{py}/A_{pa}\}_1$ as the ordinate, where the suffixes 1 and 2 correspond to the blank and the sample, and A_{py} and A_{pa}, to the peak-areas of propylene and propane, respectively. Up to 480 ppm Pd gave a straight line. Hg(II) < 1500 ppm was treated similarly; the results are shown in Fig. 4, along with those of palladium.

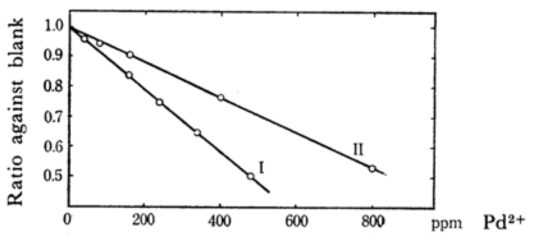

Fig. 4. Calibration curves.
I : Pd^{2+}, II : Hg^{2+}

The Effects of Diverse Ions. The effects of equimolar diverse ions on the determination of 800 μg Pd were also examined; the results obtained are shown in Table 3. As may be seen from the table, the common cations and anions almost do not interfere at all except for ferric ion, but mercuric, silver, platinous and platinic ions do interfere seriously. It is generally[2] said that the metals with eight or ten electrons in the d-orbital show a tendency to combine with olefins. The fact that no influence was observed on $Ni^{2+}(d^8)$, $Zn^{2+}(d^{10})$, and $Cd^{2+}(d^{10})$ seems to be due to the difficulties in their reduction to metals. On the other hand, the effect of the ferric ion may be attributed to the re-oxidation of palladium metal, which has been produced by the reaction with propylene.

TABLE 4. THE EFFECTS OF SILVER, PLATINOUS, MERCURIC, AND FERRIC IONS ON THE ABSORPTION

Ions	The mol ratios Pd : ions	The ratios against a blank	Pd found μg	Relative errors %
Hg^{2+}	0.5 : 1*	0.761	1166	190
Hg^{2+}	1 : 1*	0.687	1568	90.9
Hg^{2+}	1.5 : 1*	0.624	1834	52.8
Ag^+	**	0.958	—	—
Fe^{3+}	**	1.000	—	—
Pt^{2+}	**	0.956	—	—

* Pd^{2+} : 800 μg

** The amounts corresponding to 1600 μg Pd

The effects of silver, ferric, platinous, and mercuric ions on the determination of 800 μg Pd were further examined; the results are shown in Table 4. It may be seen from Tables 3 and 4 that the effects of diverse ions in the presence of palladium are much larger than those of diverse ions alone. The reaction between propylene and palladium or mercuric ions in an aqueous solution is as follows:

$$\text{propylene} + Pd^{2+} \xrightarrow{H_2O} \text{acetone} + Pd^0 \quad (1)$$

$$\text{propylene} + Hg^{2+} \xrightarrow{H_2O} \text{acrolein} + Hg_2{}^{2+} \quad (2)$$

These reactions explain satisfactorily the results in Fig. 4, in which the amount of propylene absorbed in the presence of a definite amount of palladium is approximately twice that in the presence of an equimolar mercury(II). It is also interesting to note that the amount of propylene absorbed into the mercury(II) solution in the presence of palladium ions is almost twice that absorbed in the absence of palladium ions. This suggests that either palladium metal or palladium ions might act as a catalyst to accelerate the reaction between propylene and mercurous ions. In the analysis of the reaction mixture between propylene and a mercuric solution, a large quantity of mercuric ions was detected, but no mercurous ions were detected. On the other hand, the reaction of propylene yielded a black precipitate. The precipitate was filtered off, and the filtrate was analyzed. Neither mercuric nor mercurous ions were, however, detected. When the above precipitate was dissolved in concentrated nitric acid, palladium ions were precipitated as the dimethylglyoximate. The filtrate was also analyzed, and a large quantity of mercuric ions was detected.

These results indicate that mercurous ions are reduced with propylene to form metallic mercury. On the basis of these data, the reaction between propylene and mercury(II) in either the presence or the absence of palladium ions may be supposed

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[2] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, New York (1965), p. 351.

TABLE 5. THE EFFECTS OF CHLORIDE AND BROMIDE IONS

Pd^{2+} taken: 800 μg, Acidity: 0.4 N $HClO_4$

The mole ratios					The ratios against a blank	Pd found μg	Relative errors %
Pd	Hg	Ag	Cl*	Br*			
1	1	—	—	—	0.687	1527	+90.9
1	—	—	50	—	0.852	722	−9.75
1	1	—	5	—	0.692	1502	+87.7
1	1	—	10	—	0.694	1493	+86.6
1	1	—	50	—	0.772	1112	+39.0
—	1	—	—	5	0.992	—	—
1	—	—	—	5	0.828	839	+4.88
1	1	—	—	5	0.819	883	+11.0
1	—	1	—	—	0.747	1234	+54.3
1	—	1	2.5	—	0.844	761	−4.88
1	—	5	10	—	0.828	839	+4.88
1	—	—	10	—	0.832	820	+2.50

* Sodium salts

TABLE 6. THE DETERMINATION OF PALLADIUM IN THE PRESENCE OF SILVER, MERCURIC, AND FERRIC IONS

The mole ratios						The ratios against a blank	Pd^{2+} found μg	Relative errors %
Pd	Ag	Hg	Fe	Cl	Br			
1	—	—	1	20	—	0.842	771	−3.62
1	1	1	1	—	7	0.826	849	+6.13

to proceed in accordance with the following mechanisms, (3) and (4), but not the reaction (2):

$$\text{propylene} + Hg^{2+} \xrightarrow{H_2O} [Hg^{2+}\cdot\text{propylene}] \quad (3)$$

$$[Hg^{2+}\cdot\text{propylene}] \xrightarrow{Pd} Hg^0 + Pd^0 + \text{Product} \quad (4)$$

The mercury-propylene complex may be supposed not to be hydrolyzed at 25°C, while it is subject to hydrolyzation in the presence of palladium ions. The interferences by mercury(II) and silver are eliminated by adding suitable amounts of chloride or bromide (Table 5).

The effect of iron(III) could not be removed by the use of a complexing agent, but it could be eliminated by a cation exchanger, Amberlite IR-120. The palladium ions forming a stable complex anion with chloride, they are easily separated from ferric ions by a cation exchanger. Silver, mercury, and ferric ions equimolar to 800 μg palladium were taken in a small beaker with the palladium ions, and 7 times as much sodium bromide as the moles of palladium was added. The precipitate of silver bromide was filtered off, and the filtrate was passed through an ion-exchange column to eliminate any ferric ions, The column was then washed with 20 m*l* of 1 N perchloric acid, and the combined solution was concentrated to 20 m*l*. A 5 m*l* portion was taken out of the final solution and analyzed by the gas chromatograph. The results are shown in Table 6. The authors have not yet succeeded in eliminating the interference by platinous and platinic ions.

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