# Simultaneous Injection Effective Mixing Flow Analysis System for Spectrophotometric Determination of Palladium in Dental Alloy and Catalyst

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### Abstract

A simultaneous injection effective mixing flow analysis (SIEMA) system was proposed for the spectrophotometric determination of palladium. The determination of palladium was based on its complexation reaction with 2-(5-bromo-2-pyridylazo)-5-[N-n-propyl-N-(3-sulfopropyl)amino]aniline (5-Br-PSAA) to form a blue complex, which has an absorption maximum at 612 nm. The analytical performances of the proposed SIEMA method were superior to a conventional FIA method using 5-Br-PSAA in several parameters, such as reagent consumption, waste volume and analysis time. The SIEMA method was applied to the determination of palladium in dental alloy and hydrogenation catalyst.

Keywords Simultaneous injection effective mixing flow analysis, spectrophotometry, palladium, 5-Br-PSAA

## 1. Introduction

Palladium is widely used in industrial fields: e.g. a catalyst in synthetic organic chemistry [1], a catalytic converter for automobiles [2] and a dental alloy [3]. Determination of platinum group elements, such as rhodium, palladium, platinum, etc., in their functional materials is therefore of great importance. Although ICP-AES and ICP-MS are a powerful instrumental analytical method for the determination of platinum group elements [4], flow analysis with spectrophotometry provides us with a much affordable analytical method.

In the last three decades, numerous flow analysis methods have been proposed for the spectrophotometric determination of palladium using various chromogenic reagents (Table 1) [5–21]. Most of them are flow injection analysis methods, and they have been applied to the determination of palladium in catalysts, ores, metallurgical samples, etc. A few papers on stopped flow analysis of palladium were reported by Anthemidis et al. [14,16]. One of the author (T. S.) proposed a FIA method for highly sensitive determination of palladium, based on its complexation reaction with a water soluble chromogenic reagent: 2-(5-bromo-2-pyridylazo)-5-[*N-n*-propyl-*N*-(3-sulfopropyl) amino]aniline (5-Br-PSAA) [6].

We described a novel concept of simultaneous injection-effective mixing flow analysis (SIEMA), and a three-channel SIEMA method applied to the spectrophotometric determination of palladium using 5-Br-PSAA was demonstrated [20]. Since then, SIEMA methods for the determinations of urinary bilirubin [22], residual chlorine in tap water [23], urinary albumin [24], urinary bilirubin and urobilinogen [25], urinary bilirubin and creatinine [26] have been reported. Also, we described the characteristics of SIEMA in a mini-review [27].

In a previous rapid communication [20], the reagent (5-Br-PSAA) consumption of the SIEMA  $(6.0 \times 10^{-8} \text{ M})$  was less than that of the FIA method [6]  $(1.6 \times 10^{-7} \text{ M})$ . However, the analytical time of the SIEMA for one analysis (82 s) was slower than that of FIA (64 s). The worse performance on rapidity was caused by sequential (stepwisely) aspiration procedures of three solutions of sample, reagent and buffer into the individual

holding coils.

In this work, we modified the SIEMA protocol; i.e. the three solutions were simultaneously aspirated into each holding coils, so that the rapidity was improved. Furthermore, optimization studies were carried out with the modified protocol. As a result, we obtained better analytical performances on not only rapidity but also lower reagent consumption and less waste generation compared with a conventional FIA method [6]. The improved SIEMA method was applied to the determination of palladium in dental alloy and hydrogenation catalyst.

### 2. Experimental

#### 2.1. Reagents

All reagents used were of analytical grade, and de-ionized water purified by an Aquarius GSH-210 (Advantec, Tokyo) was used throughout.

A stock standard solution (100 mg L<sup>-1</sup>) of palladium was prepared by 10-fold dilution of commercially available 1000 mg L<sup>-1</sup> palladium(II) standard solution for atomic absorption spectrometry (Wako, Osaka) with water. Working solutions were prepared daily by diluting the stock solution with 0.1 mol L<sup>-1</sup> nitric acid.

A  $3.0 \times 10^{-3}$  mol L<sup>-1</sup> 5-Br-PSAA stock solution was prepared by dissolving 0.1435 g of 2-(5-bromo-2-pyridylazo)-5-[*N-n*-propyl-*N*-(3-sulfopropyl)amino]aniline, sodium salt (Dojindo, Kumamoto) in 100 mL of water and was stored in a dark container. The stock solution was daily diluted to 10-fold with water to prepare a  $3.0 \times 10^{-4}$  mol L<sup>-1</sup> 5-Br-PSAA, which was aspirated from a reservoir bottle in the SIEMA system (Fig. 1).

An acetate buffer solution (pH 4.5) at a concentration of 0.2 mol  $L^{-1}$  was prepared by mixing appropriately solutions of acetic acid (Sigma-Aldrich Japan, Tokyo) and sodium acetate trihydrate (Nacalai Tesque, Kyoto).

#### 2.2. Apparatus

The SIEMA system shown in Fig. 1 basically consisted of a bidirectional syringe pump (SP) with a syringe pump valve (SPV), three 3-way solenoid valves  $(3SV_1-3SV_3)$  and a 2-way solenoid valve (2SV), which were controlled by homemade

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Flow	Chromogenic reagent	Dynamic range	Application <sup>c</sup>	Reference
system <sup>a</sup>		$/ \text{ mg } L^{-1}$		No.
FIA	EDTA	4.2-17	N.A.	5
FIA	5-Br-PSAA	0.01-0.1	Dental alloy,	6
			automobile exhaust	
			gas converter	
FIA	Sulfochlorophenolazorhodanine	0.045-30.0	N.A.	7
FIA	DCS-arsenazo	0-8.0	Metallurgical sample	8
FIA	1,8-dihydroxy-2-(4-chloro-2-phosphonophenylazo)-7-(6,8-di	1–3	Pt-Pd refined ore	9
	sulphonaphthylazo)naphthalene			
FIA	1,8-dihydroxy-2-(4-chloro-2-phosphonophenylazo)-7-(4-sulp	1–4	Pt-Pd refined ore	9
	honamidophenyl-azo)-3,6-disulphonaphthalene			
FIA	1,8-dihydroxy-2-(4-chloro-2-phosphonophenylazo)-7-(p-hipp	1–5	Pt-Pd refined ore	9
	uric acid azo)-3,6-disulphonaphthalene			
FIA	Tin(II) chloride	5-600	N.A.	10
FIA	Chlorophosphonazo-mN	2-10	Anode mud	11
FIA	5-Cl-PADAB	2.0-10.0	N.A.	12
FIA	Dibromo-o-carborylchlorophosphonazo	0.1-3.2	Catalyst, anode mud	13
SFA	2,2'-dipyridyl-2-pyridylhydrazone	0–60	Hydrogenation	14
			catalyst, automobile	
			exhaust gas	
			converters catalyst	
FIA	Chlorophosphonazo-p-Cl	1.0-17.0	Ore, catalyst	15
SFA	2,2'-dipyridyl-2-pyridylhydrazone	0-12	automobile exhaust	16
			gas converters	
			catalyst	
FIA	Thiocyanate	5-22.5	N.A.	17
FIA	Tin(II) chloride	3.0-32	Pharmaceuticals,	18
			industrial catalysts	
FIA	N-phenylbenzimidoylthiourea	0.25-10	Catalyst	19
SIEMA	5-Br-PSAA	0–4	N.A.	20
FIA	2,2'-Furyldioxime	0.01-10.0	catalytic converter,	21
			anodic slime, road	
			sediment, ore, water	
SIEMA	5-Br-PSAA	0-1	Dental alloy,	This work
			hydrogenation	
			catalyst	

 Table 1
 Flow analysis methods for the spectrophotometric determination of palladium

a. FIA: flow injection analysis; SFA: stopped flow analysis; SIEMA: simultaneous injection effective mixing flow analysis.

b. 5-Br-PSAA: 2-(5-Bromo-2-pyridylazo)-5-[*N-n*-propyl-*N*-(3-sulfopropyl)amino]aniline;

DCS-arsenazo: 2-[(2-Arsonophenyl)azo]-1,8-dihydroxy-7-(4-sulfo-2,6-dichlorophenylazo)naphthalene-3,6-disulfonic acid; 5-Cl-PADAB: 4-(5-chloro-2-pyridylazo)-1,3-diaminobenzene.

c. N.A.: not available.

software in a laptop computer. A double beam spectrophotometer (S-3250, Soma Optics) fitted with a flow-through cell (8  $\mu$ L volume, 10 mm path length) was used for absorbance measurement. The detector output was acquired on a PC through an A/D converter (Chromato-Pro, RTC, Sagamihara, Japan). All flow lines were built using 0.8 mm i.d. Teflon tubing except for the auxiliary coil (AC) having inner diameter of 2 mm.

### 2.3. Procedure

The temporal operation of the SIEMA system is given in Table 2. In step 1, a palladium(II) standard/sample, 5-Br-PSAA and acetate buffer (the total volume was 300  $\mu$ L) were simultaneously aspirated into each holding coil (HC<sub>1</sub>, HC<sub>2</sub> and HC<sub>3</sub>) via each 3-way solenoid valve (3V<sub>1</sub>, 3V<sub>2</sub> and 3V<sub>3</sub>). While aspirating them, the 2-way solenoid valve (2SV) was turned off for selective aspiration with accurate volume via 3-way solenoid valves (to avoid aspiration of fluid from the downstream). In step 2, a 1200  $\mu$ L of carrier water was aspirated into syringe (the total



Fig. 1 Schematic diagram of the SIEMA for palladium determination. CS, water; S, standard/sample; R,  $3.0 \times 10^{-4}$  mol L<sup>-1</sup> 5-Br-PSAA; B, 0.2 mol L<sup>-1</sup> acetate buffer (pH 4.5); SP, syringe pump; SPV, syringe pump valve atop SP; AC, auxiliary coil (2 mm i.d., 0.65 m long); C<sub>1</sub> and C<sub>2</sub>, 4-way cross connector; HC<sub>1</sub>, HC<sub>2</sub> and HC<sub>3</sub>, holding coils;  $3SV_1$ ,  $3SV_2$  and  $3SV_3$ , 3-way solenoid valves; 2SV, 2-way solenoid valve, MC, mixing coil (0.8 mm i.d., 0.6 m long); D, spectrophotometer (612 nm); AD, A/D converter; PC, computer; W, waste.

Table 2 Temporal operation of the SIEMA system

Step	SPV	Motion direction of SP	3SV <sub>1</sub>	3SV <sub>2</sub>	3SV <sub>3</sub>	2SV	Flow rate / $\mu L s^{-1}$	Time / s <sup>a</sup>	Function
1	ON	$\downarrow$	ON	ON	ON	OFF	50	6	Simultaneous aspiration of palladium(II) standard/sample, 5-Br-PSAA and acetate buffer into HC <sub>1</sub> , HC <sub>2</sub> and HC <sub>3</sub> , respectively
2	OFF	$\downarrow$	OFF	OFF	OFF	OFF	300	4	Aspiration of carrier water into syringe
3	ON	<b>↑</b>	OFF	OFF	OFF	ON	50	30	Dispensing all aspirated zones to detector simultaneously

a. The sum of working times was 40 s (= 6 + 4 + 30), but the system needed 8 s for switching of valves. The total analysis time was eventually 48 s per one determination.



Fig. 2 Effect of 5-Br-PSAA concentration on the responses of (a) blank, (b) 0.5 mg  $L^{-1}$  palladium(II) and (c) net absorbance ((b) minus (a)).



Fig. 4 Effect of total aspiration volume on the responses of (a) blank, (b) 0.5 mg  $L^{-1}$  palladium(II) and (c) net absorbance ((b) minus (a)).

volume of water in the syringe was eventually 1500  $\mu$ L). Then, all solutions in the three holding coils were simultaneously dispensed to be merged at a confluence point (C<sub>2</sub>). After the confluence point, an effective mixing condition was obtained, and therefore complex formation took place successfully in the mixing coil (MC). The absorbance of the colored product was measured with a spectrophotometric detector at 612 nm.



Fig. 3 Effect of pH on the responses of (a) blank, (b) 0.5 mg  $L^{-1}$  palladium(II) and (c) net absorbance ((b) minus (a)).

### 3. Results and discussion

### 3.1. Optimization

The experimental conditions for 5-Br-PSAA concentration, pH, aspiration volume and mixing length were studied for the determination of 0.5 mg  $L^{-1}$  palladium(II).

# 3.1.1. Effect of 5-Br-PSAA concentration

The concentration of 5-Br-PSAA was varied in the range of  $1.5-5.0\times10^{-4}$  mol L<sup>-1</sup>. The result is shown in Fig. 2. The responses of blank (a) and palladium(II) (b) increased with increasing the 5-Br-PSAA concentration. At the concentrations greater than  $3.0\times10^{-4}$  mol L<sup>-1</sup>, the net absorbance (c) change was moderate. In this study, a 5-Br-PSAA concentration of  $3.0\times10^{-4}$  mol L<sup>-1</sup> was chosen.

### 3.1.2. Effect of pH

The effect of pH on the responses was examined by changing the buffer solution. The results is shown in Fig. 3. The x-axis of Fig. 3 stands for the pH of the waste solution. The net absorbance became substantially flat in the pH range of 2.6 to 3.0. The absorbance of the blank was lower as the pH was increasing. Therefore, a pH value of 3.0 was selected to obtain a high net absorbance.



Fig. 5 Effect of mixing coil length on the responses of (a) blank, (b) 0.5 mg  $L^{-1}$  palladium(II) and (c) net absorbance ((b) minus (a)).

Table 3 Comparison of the analytical performances between this work and FIA [6]

Parameter	This work	FIA [6]	
Reagent consumption /	$3.0 \times 10^{-8}$	1.6×10 <sup>-7</sup>	
one determination in mol	5.0×10		
Waste volume /	15	21	
ten determinations in mL	15		
Time taken /	19	64	
one determination in sec	40		
Linear range	0.1.0	0-0.1	
in mg L <sup>-1</sup> palladium(II)	0-1.0		
Linear regression equation <sup>a</sup>	$A = 0.101 C_{\rm Pd}$	$A = 0.181C_{\rm Pd}$	
Regression coefficient	0.998	0.999	
$3\sigma$ limit of detection in µg	1.0	2.0	
$L^{-1}$	1.8	2.0	
Repeatability (RSD%) for	1 0 b	0.6 %	
$0.1 \text{ mg L}^{-1}$	1.0 *	0.6	

a. A, net absorbance;  $C_{Pd}$ , palladium(II) concentration in mg L<sup>-1</sup>.

### 3.1.3 Effect of aspiration volume

Three solutions of standard, 5-Br-PSAA and buffer were aspirated simultaneously. The total aspiration volume was varied in the range of 150–600  $\mu$ L. As shown in Fig. 4, the responses increased monotonically. In order to save the reagent consumption, we chose a total volume of 300  $\mu$ L (theoretically, each solution of 100  $\mu$ L is aspirated).

# 3.1.4. Effect of mixing coil length

The length of the mixing coil was varied in the range of 0.3-1.2 m (Fig. 5). At a coil length longer than 0.6 m, it was difficult to push the solution to the end of the flow line. We chose therefore a coil length of 0.6 m.

#### 3.2. Analytical performances

A typical calibration sequence is shown in Fig. 6. A good linearity was obtained by its linear equation (net absorbance =



Fig. 6 Typical system outputs for palladium(II) standards. Concentrations of palladium(II) in mg  $L^{-1}$ : (a), 0; (b), 0.10; (c), 0.25; (d), 0.50; (e), 0.70; (f), 1.00.

Table 4 Tolerance limits on the determination of 0.5 mg  $L^{-1}$  palladium(II)

Panaaran(11)	
Tolerance	Ion added
$/ \text{ mg } L^{-1}$	
500	Cd(II), Pb(II), Se(IV), Br <sup>-</sup> , Cl <sup>-</sup> , NO <sup>-</sup>
200	Fe(III)
100	Ni(II), Zn(II)
50	Al(III), In(III)
20	Rh(III)
10	Fe(II)
5	Ag(I), Co(II)
0.5	Au(III), Pt(IV)
0.02	Cu(II)

0.101[palladium(II) in mg L<sup>-1</sup>]) with a correlation coefficient ( $r^2 = 0.998$ ). We compared the analytical performances between SIEMA in this study and the FIA reported by one of the authors [6]. As summarized in Table 3, the sensitivity and repeatability between these two methods are comparable. However, the time taken per one analysis by SIEMA is shorter than that of FIA. Also, the 5-Br-PSAA consumption of the proposed system is less than in FIA method. Furthermore, we could reduce waste generation.

### 3.3. Interferences

Different ions were added to a 0.5 mg  $L^{-1}$  palladium(II) standard solution. The effects of the coexisting substances were considered to be tolerable within  $\pm 5\%$ . The results are shown in Table 4. Copper(II) showed the largest interference, since 5-Br-PSAA reacts with copper(II) to form a colored complex [28]. We decided that this method should be applied to real samples, which did not include large amount of copper(II) shown below.

3.4. Determination of palladium in dental alloy and hydrogenation catalyst

The proposed SIEMA was applied to the determination of palladium in dental alloy and in palladium carbon as hydrogenation catalyst. Sample solutions were prepared as

b, n = 5.

c. n = 10.

		Prop	ICP-MS			
Sample	Added	Found	Recovery	Pd content in sample	Found	Pd content in sample
	$/ \text{ mg } \text{L}^{-1}$	/ mg L <sup>-1 a</sup>	/ %	$/ \text{ mg } L^{-1}$	/ mg L <sup>-1 a</sup>	$/ \text{ mg } \text{L}^{-1}$
Dental alloy <sup>b</sup>	0	0.191	_	9.5	$0.200 \pm 0.003$	9.9±0.15
	0.10	0.291	100	9.5		
	0.25	0.440	100	9.4		
	0.50	0.702	102	10		
				Ave. 9.6±0.2 <sub>7</sub>		
Palladium carbon <sup>c</sup>	0	0.213	_	10.3	0.200±0.003	9.7±0.15
	0.1	0.313	100	10.3		
	0.25	0.459	98.5	10.1		
				Ave. 10.2±0.1 <sub>1</sub>		

Table 5 Analytical results for palladium in dental alloy and hydrogenation catalyst

a. Values obtained from each calibration curve. These values were used to calculate the Pd content in the samples.

b. Contains 68% of Ag, 10% of Pd, 17% of In and others (5%).

c. Contains 10% of Pd.

follows. A 0.5 g sample of dental alloy was dissolved in 10 mL of nitric acid, the solution was evaporated to dryness, and the residue was dissolved in 4.2 mL of hydrochloric acid and 20 mL of water by heating. After filtration, the filtrate was diluted with water to the mark in a 100-mL volumetric flask. For palladium carbon, a 0.1 g of sample was dissolved in 10 mL of aqua regia, the resulting solution was evaporated to dryness, and the residue was treated as described above. The decomposed sample solutions were suitably diluted with 0.1 mol  $L^{-1}$  hydrochloric acid before introduction into the SIEMA system.

The results obtained by the proposed method and by ICP-MS are summarized in Table 5. Recoveries of spiked palladium were satisfactory. Also, the palladium content values obtained by the proposed method were in good agreement with those obtained by ICP-MS and with the labeled values.

### 4. Conclusion

We have described here a SIEMA method for the determination of palladium in dental alloy and hydrogenation catalyst with good accuracy. The SIEMA system reduced the reagent consumption, waste generation and analysis time compared with a conventional FIA. The SIEMA system can be applied to other chemical analysis.

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