

# Spectrophotometric Determination of Hafnium with Semimethylxlenol Blue

メタデータ	言語: eng 出版者: 公開日: 2017-10-03 キーワード (Ja): キーワード (En): 作成者: メールアドレス: 所属:
URL	<a href="http://hdl.handle.net/2297/20570">http://hdl.handle.net/2297/20570</a>

## Spectrophotometric Determination of Hafnium with Semimethylxylenol Blue

Joichi UEDA, Shiro KOSUMI and Shigehiro KAGAYA

*Department of Chemistry, Faculty of Education, Kanazawa University, Marunouchi, Kanazawa, 920, Japan*

**Summary**—Semimethylxylenol Blue (SMXB) reacts sensitively with hafnium and forms a water-soluble red complex. The colored solution shows a maximum and definite absorbance at the wavelength range from 577 to 579 nm and at the pH range 1.4–2.1. Beer's law is obeyed up to 2.0  $\mu\text{g/ml}$  of hafnium, and the sensitivity of the determination is  $2.0 \times 10^{-3} \mu\text{g/cm}^2$  of hafnium for  $\log(I_0/I) = 0.001$  at 578 nm. Among the forty-four diverse ions examined, gallium, bismuth(III), zirconium, thorium, iron(III), and fluoride interfere with the determination. But the effect from iron(III) is eliminated with ascorbic acid and the interference of bismuth(III) can be removed by filtration of bismuth(III) as the precipitate of its oxide compound.

### INTRODUCTION

In a series of the sulfophthalein derivatives, there are many useful compounds utilized as the spectrophotometric reagents for various metal ions.<sup>1,2</sup> Semimethylxylenol Blue, 3-[N, N-di(carboxymethyl)aminomethyl]-*p*-xylenolsulfophthalein, SMXB, is one of the sulfophthalein derivatives which is obtained as a by-product in the synthesis of Methylxylenol Blue, 3, 3'-bis [N, N-di(carboxymethyl)aminomethyl]-*p*-xylenolsulfophthalein, MXB, by the Mannich condensation<sup>1</sup> and is expected to be as an useful spectrophotometric reagent as MXB. In the previous papers,<sup>3-7</sup> the authors proposed the spectrophotometric methods for the determination of a few metal ions using SMXB. This reagent also reacts with hafnium in acidic medium to form a water-soluble red complex. So, in this work, the fundamental conditions for the spectrophotometric determination of hafnium based on this color reaction were examined, and it was found that SMXB is suitable reagent for the determination of hafnium, because the reaction is very sensitive giving stable coloration and has relatively good selectivity.

Comparing the present method with other photometric methods which utilize the water-soluble complex of hafnium, SMXB is less sensitive than Arsenazo III<sup>8</sup> which is representative photometric reagent for hafnium. However, the present method has higher sensitivity than the methods using such reagents with similar structures to SMXB as Xylenol Orange and Methylthymol Blue<sup>9</sup> and is nearly as specific as those methods. Further, SMXB is more sensitive than other many reagents such as Morin,<sup>10</sup> Chromazurol S,<sup>11</sup> 3-nitroalizarin,<sup>12</sup> 3,4-dihydroxyazobenzene,<sup>13</sup> 3-hydroxy-2-naphthoylhydrazone,<sup>14</sup> and Bromopyrogallol Red or 4-(2-

pyridylazo)resorcinol in the presence of cationic surfactants.<sup>15,16</sup> Recently, the sensitive methods which use *o*-hydroxyhydroquinonephthalein or 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol in the presence of cationic surfactants<sup>17,18</sup> have been proposed, giving nearly as high sensitivity as Arsenazo III. However, it seems that those two methods are less specific than the present method. This paper describes the fundamental conditions for the spectrophotometric determination of hafnium utilizing SMXB as the photometric reagent.

## EXPERIMENTAL

### Reagents

Standard hafnium solution : A solution containing about 1 mg/ml of hafnium was prepared by dissolving hafnium chloride (Nakarai Chemicals) in 2M hydrochloric acid. The solution was standardized by complexometric back titration with a standard solution of thorium using Xylenol Orange as an indicator and diluted with 2M hydrochloric acid as required.

SMXB solution : SMXB was synthesized from Paraxylenol Blue, iminodiacetic acid, and formaldehyde by the Mannich condensation, separated from the reaction mixture on a cellulose column by 1-butanol saturated with 0.1% acetic acid, and then obtained in the free acid form by passing the fraction of SMXB through a column of cation-exchange resins.<sup>1,3</sup> A 0.1% SMXB solution was then prepared by dissolving a weighed amount of the SMXB in distilled water.

2M hydrochloric acid and 2M ammonium acetate were used for pH adjustment.

All the other reagents used were of guaranteed reagent grade.

### Apparatus

A Hitachi-Perkin-Elmer model 139 spectrophotometer with 1 cm glass cells was used for the absorbance measurements, and a Hitachi-Horiba model M-5 glass electrode pH meter for the pH measurements.

### Recommended procedure

A sample solution containing up to 50  $\mu\text{g}$  of hafnium is taken into a 25 ml volumetric flask and 3 ml of 0.1% SMXB solution is added. Then, the pH of the solution is adjusted to 1.5 in the final pH with 2M ammonium acetate or 2M hydrochloric acid solution. After making up the volume to 25 ml, the absorbance is measured at 578 nm against reagent blank.

## RESULTS AND DISCUSSION

### Absorption spectra

Figure 1 shows the absorption curve of hafnium-SMXB complex which was measured against the reagent blank according to the recommended procedure. A wavelength of 578 nm is suggested for the measurements since the absorption maximum of the colored solution is at 577-579 nm.

### The effect of pH

The effect of pH on absorbance of the complex was investigated, changing the pH of the solution at various values with 2M hydrochloric acid or 2M ammonium acetate solution. As shown in Fig. 2, the range in which the maximum and almost constant absorbance was obtained was pH 1.4-2.1. The almost same results were also obtained when sodium acetate or sodium hydroxide was used for the pH adjustments instead of ammonium acetate.

### The effect of the addition of SMXB

The amount of 0.1% SMXB was varied to investigate the effect of the reagent concentration on the absorbance. The maximum color formation was obtained by adding from 2 to 5 ml of reagent solution for 0.8  $\mu\text{g}/\text{ml}$  of hafnium.

### The stability of the color

The color reaction with hafnium and SMXB was rapid at a room temperature and the full color development occurred immediately after the reagent was added. The color, once developed, was very stable and the absorbance remained almost constant for at least 4 hrs.

### Calibration curve

According to the recommended procedure, the calibration curve for hafnium was prepared. A straight line passing through the origin was obtained over the concentration range 0.2-2.0  $\mu\text{g}/\text{ml}$  of hafnium. The apparent molar absorptivity of the colored solution and the sensitivity of the determination which were calculated from the curve were  $8.95 \times 10^4 \text{ l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$  and 0.002  $\mu\text{g}$  Hf/ $\text{cm}^2$  for  $\log(I_0/I)=0.001$ , respectively. The relative standard deviation for five replicate determinations was 0.48% for 0.8  $\mu\text{g}/\text{ml}$  of hafnium.

### The composition of the complex

The composition of the hafnium-SMXB complex was examined at pH 1.5 by the mole ratio

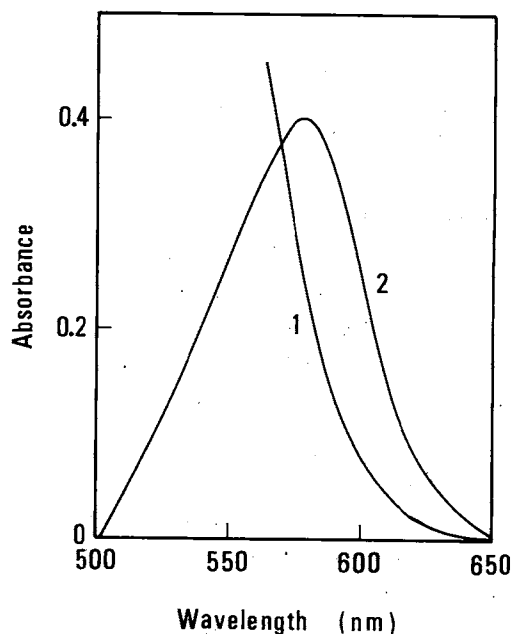


Fig. 1. Absorption spectra ; (1) reagent blank vs. water ; (2) Hf, 20  $\mu\text{g}/25\text{ml}$  vs. reagent blank ; 0.1% SMXB, 3ml/25ml ; pH, 1.5.

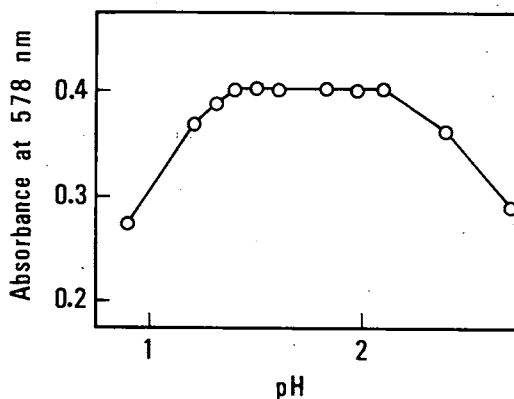


Fig. 2. Effect of pH ; Hf, 20  $\mu\text{g}/25\text{ml}$  vs. reagent blank ; 0.1% SMXB, 3ml/25ml.

and the continuous variation methods, measuring the absorbance at the wavelengths, 560, 578, and 600 nm. In the former method, various amounts of SMXB were added to a constant amount of hafnium,  $8.96 \times 10^{-6} \text{M}$ , and in the latter method, the total moles of hafnium and SMXB was held constant at  $3.59 \times 10^{-5} \text{M}$ .

The result that a 1 : 2 complex is formed between hafnium and SMXB was obtained by the measurements at 578 nm. At another wavelengths, however, it was recognized that the maximum point of the absorbance in the continuous variation method and the equivalence point in the mole ratio method were shifted from the points which indicate the formation of a 1 : 2 hafnium-SMVB complex. So, it seems that the hafnium-SMVB complex is not only a composition(1 : 2), but it is probably present as a mixture of more than two kinds of complexes with different composition.

### The effect of diverse ions

The effect of 44 diverse ions on the determination of 20  $\mu\text{g}$  of hafnium was examined by the recommended procedure. As the results were summarized in Table 1, 23 cations such as alkali metals, alkaline earth metals, lead, zinc, lanthanoids, chromium(III), manganese(II), nickel, and cobalt did not interfere with the determination, even if they were present at a concentration of 50 times that of hafnium. Some anions such as tartrate and citrate could also coexist, at least up to 500 times of the amount of hafnium. The presence of gallium, bismuth(III), zirconium, thorium, iron(III), and fluoride, however, interfered with the determination seriously. But the effect from iron(III) was eliminated with ascorbic acid and the interference of bismuth(III) could be removed by the filtration of bismuth(III) as the precipitate of its oxide compound.

Table 1. Effect of diverse ions on the determination of 20  $\mu\text{g}$  of hafnium in 25 ml

Ion	Amount added* (mg)	Hafnium found† ( $\mu\text{g}$ )	Ion	Amount added* (mg)	Hafnium found† ( $\mu\text{g}$ )
Li <sup>+</sup>	1	19.7	Ce <sup>3+</sup>	1	20.1
K <sup>+</sup>	1	20.3	Ti <sup>4+</sup>	0.1	19.5
Be <sup>2+</sup>	1	20.7	Zr <sup>4+</sup>	0.01	40.2
Mg <sup>2+</sup>	1	20.1	Th <sup>4+</sup>	0.02	24.9
Ca <sup>2+</sup>	1	20.1	V(V)	0.02	20.7
Sr <sup>2+</sup>	1	20.3	Cr <sup>3+</sup>	1	20.5
Ba <sup>2+</sup>	1	20.2	Mo(VI)	0.02	20.9
Al <sup>3+</sup>	0.2	20.6	W(VI)	0.02	19.9
Ga <sup>3+</sup>	0.02	26.1	UO <sub>2</sub> <sup>2+</sup>	1	20.4
In <sup>3+</sup>	0.5	20.4	Mn <sup>2+</sup>	1	20.0
Sn <sup>4+</sup>	0.02	20.9	Fe <sup>3+</sup>	0.02	49.7
Pb <sup>2+</sup>	1	19.9	" #	1	19.6
As(V)	0.1	20.0	Co <sup>2+</sup>	1	19.7
Sb <sup>3+</sup>	0.1	20.5	Ni <sup>2+</sup>	1	20.0
Bi <sup>3+</sup>	0.02	26.3	Rh <sup>3+</sup>	1	20.3

" §	1	20.1	Pb <sup>2+</sup>	0.1	20.4
Cu <sup>2+</sup>	0.02	20.0	Ir <sup>4+</sup>	0.5	19.5
Au <sup>3+</sup>	1	20.0	Pt(IV)	1	20.5
Zn <sup>2+</sup>	1	20.0	F <sup>-</sup>	0.02	15.5
Cd <sup>2+</sup>	1	20.3	PO <sub>4</sub> <sup>3-</sup>	0.05	19.8
Hg <sup>2+</sup>	1	20.7	SO <sub>4</sub> <sup>2-</sup>	1	20.0
Y <sup>3+</sup>	1	20.3	Tartrate	10	19.9
La <sup>3+</sup>	1	20.0	Citrate	10	19.8

\* Amount added per 25 ml.

† Mean of duplicate determinations.

§ Color development was made at pH 1.9, and the absorbance was measured after filtration of precipitate of bismuth(III) chloride oxide.

# 3 ml of 4% ascorbic acid solution was added.

## CONCLUSIONS

From this study, Semimethylxylenol Blue is recommended as a photometric reagent for the determination of hafnium in water samples. The sensitivity of the method is  $2.0 \times 10^{-3} \mu\text{g}/\text{cm}^2$  of hafnium for  $\log(I_0/I) = 0.001$  at 578 nm and Beer's law is obeyed up to  $2.0 \mu\text{g}/\text{ml}$  of hafnium.

From an introductory study, it was also recognized that this reagent is useful as a metallochromic indicator for a chelatometric titration of hafnium in acidic media. The details about this and the applications of Semimethylxylenol Blue in chelatometric titration will be reported soon.

## REFERENCES

1. M. Otomo, *Bunseki Kagaku*, 1972, **21**, 436.
2. V. N. Tikhonov, *Zh. Anal. Khim.*, 1977, **32**, 1435.
3. J. Ueda, *Nippon Kagaku Kaishi*, 1977, 350.
4. Idem, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 773.
5. Idem, *Nippon Kagaku Kaishi*, 1979, 1115.
6. J. Ueda and T. Kitadani, *ibid.*, 1982, 1914.
7. J. Ueda and K. Kadowaki, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1968.
8. O. Kamimori, I. Taguchi and R. Komiya, *Bunseki Kagaku*, 1965, **14**, 249.
9. A. K. Mukherji, *Analytical Chemistry of Zirconium and Hafnium*, p. 77, Pergamon Press, New York, 1970.
10. Y. Hoshino, *Nippon Kagaku Zasshi*, 1960, **81**, 1278.
11. Y. Horiuchi and H. Nishida, *Bunseki Kagaku*, 1967, **16**, 20.
12. A. T. Pilipenko and E. G. Skorokhod, *Zh. Anal. Khim.*, 1979, **34**, 126.
13. O. M. Vilkova and V. M. Ivanov, *Zh. Anal. Khim.*, 1979, **34**, 720.
14. M. C. Gutierrez, A. Gomez-Hens and M. Valcarcel, *Mikrochim. Acta*, 1984, **III**, 17.
15. Q. Xu, *Huaxue Shiji*, 1984, **6**, 191; *Anal. Abstr.*, 1985, **47**, 6B88.
16. I. Mori, Y. Fujita, K. Fujita, S. Kitano and T. Kotake, *Bunseki Kagaku*, 1986, **35**, 136.
17. M. Yamazaki, I. Mori, Y. Fujita, S. Kitano and Y. Kamada, *Bunseki Kagaku*, 1984, **33**, 170.
18. G. V. Rathaiiah and M. C. Eshwar, *Anal. Lett.*, 1986, **19**, 713.