

# Ultraviolet Spectrophotometric Simultaneous Determination of Iron, Lead, and Bismuth by Hydrochloric Acid

Yuroku YAMAMOTO\*

(Ishibashi Laboratory)

*Received October 21, 1958*

The ultraviolet spectrophotometric determination of iron, lead, and bismuth was studied. In the hydrochloric acid medium these metals exist as chloro-complex ions. The absorption spectra were investigated with hydrochloric acid concentration, and the bathochromic effect was observed when the chloride ion was increased. The calibration curve was made for each element at the peak of absorption in 6 *M* hydrochloric acid. For the mixed sample solution of these elements in various concentrations, the simultaneous determination was attempted under the optimum condition studied. The mean errors for the determination were 3.2% for iron, 2.2% for lead, and 1.2% for bismuth in the range of 2.0-10.0 p.p.m. in various concentrations. The proposed method of determination of these elements is simple in procedure having a high sensitivity comparable to that of other common spectrophotometric method.

## INTRODUCTION

The absorptiometric determination of metal using mineral acid is convenient and useful so that no special reagent such as organic reagent is needed.

Several works have recently been reported on the methods using mineral acid such as hydrochloric,<sup>1)</sup> hydrobromic,<sup>2)-5)</sup> sulfuric,<sup>6)7)</sup> and perchloric acid.<sup>8)</sup> In the studies to establish a series of the ultraviolet spectrophotometric determination of metallic ions, we have already reported the methods for determining iron (III),<sup>9)-12)</sup> lead,<sup>13)</sup> and bismuth<sup>14)</sup> in which sulfuric,<sup>9)</sup> perchloric,<sup>10)</sup> hydrochloric,<sup>11)</sup> and acetic acids<sup>12)</sup> were used as reagents. In these methods, the absorbance of the solution was measured at maximum wave length of absorption band which may be due to the complexes formed between metallic ion and anion such as sulfate, hydroxyl, chloride, and acetate ion.

Appreciable interferences were found in the cases when several metallic ions such as iron, lead, bismuth, tin, and antimony were present. In such cases, however, it is able to determine some of these elements simultaneously by a simple procedure which has been derived in the author's article on the method of the simultaneous determination of iron (III), lead, and bismuth by perchloric acid.<sup>15)</sup> Merrit and co-workers,<sup>16)</sup> on the other hand, provided the method of simultaneous determination of bismuth, lead, and thallium based on the measurement of absorbance in the hydrochloric acid.

In the present paper results are dealt with the study of the determination of iron, lead, and bismuth using the hydrochloric acid as reagent.

---

\* 山本勇麿

## EXPERIMENTAL AND RESULT

## Apparatus and Materials

Spectrophotometric measurements were made with a Beckman Quartz Spectrophotometer, Model DU, with 1 cm silica transmission cells.

All solutions were prepared from pure reagent and distilled water. Standard stock solution of the elements whose spectra were to be studied was prepared by dissolving the required weight of pure metal or compound in an appropriate concentration of acid. The stock solution of iron (III) was prepared as follows. Ferric perchlorate was formed by dissolving proper amounts of electrolytic iron in perchloric acid (about 4 *N*), oxidizing by hydrogen peroxide (3%) and evaporating the solution until crystals appear. After perchloric acid was added to dissolve the deposit, the solution was evaporated almost to dryness. The procedure was repeated several times. The resulting solution was diluted with 0.1 *M* perchloric acid to the concentration of 100 p.p.m. The lead (or bismuth) stock solution was also obtained as the solution of perchlorate by the above described method for the solution of iron after lead acetate (or metallic bismuth) was dissolved in nitric acid. The absence of iron (III) or chloride ion was also confirmed for all the solutions by thiocyanate or silver nitrate.

## Absorption Spectra

All the solutions for absorbance measurement were prepared by dilution of the required quantity of the stock solution. Aliquot amounts of the stock solution were transferred with pipette into the volumetric flask. After adding the proper amounts of the concentrated hydrochloric acid, the solution was diluted to the concentration of 10.0 p.p.m. by distilled water.

All the spectra were obtained, as shown in Figs. 1 and 2, in the range from 210  $m\mu$  to 300  $m\mu$  with respect to the reference solution of equivalent concentration of hydrochloric acid. In both figures, it is observed that a position of maximum absorption shifts to a longer wave length as the concentration of

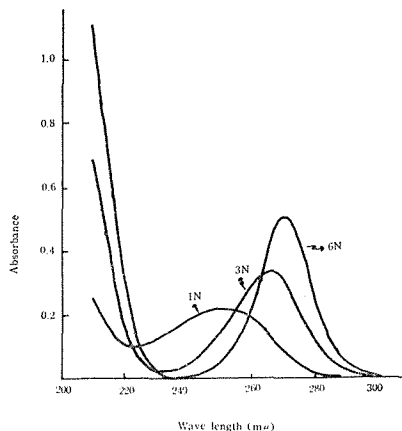


Fig. 1. Absorption spectra of  $Pb^{++}$  in HCl  
Pb : 10 p.p.m.

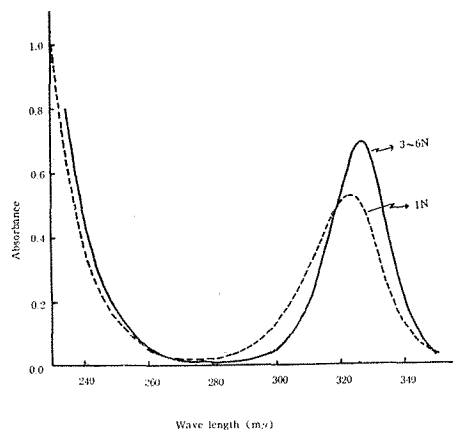


Fig. 2. Absorption spectra of  $Bi^{+++}$  in HCl.  
Bi : 10 p.p.m.

## Determination of Iron, Lead and Bismuth

hydrochloric acid increases. For instance, in 1 *M* hydrochloric acid solution the maximum absorption is shown at 252 *mμ* for lead and at 324 *mμ* for bismuth, but the maximum of lead shifts to 270 *mμ* and that of bismuth to 327 *mμ* when the acid concentration is increased to 6 *M*. Generally, the absorbance is also affected by the variation of hydrochloric acid concentration; it increases increasing the acid concentration. In the range of 3~6 *M* of hydrochloric acid, especially in the case of bismuth however, the absorbance remains almost constant even when the acid concentration is changed. The degree of change in absorbance is small in the case of lead. For the determination of lead and bismuth, therefore, it is desirable to use a highest possible concentration of hydrochloric acid.

Since it is usual that increase in the concentration of ligand brings about bathochromic effect, it may be entirely attributed to the successive formation from lower to higher chloro-complex that the position and the intensity of the absorption maxima varied with the hydrochloric acid concentration. According to Merrit,<sup>16)</sup> the factor by which the absorbance intensity of bismuth or lead solutions mainly influenced is not the acidity but the chloride concentration. It may be possible, therefore, to use the other chloride such as sodium chloride or calcium chloride as reagent instead of hydrogen chloride. In any case, it is necessary to hold the concentration of chloride ion constant in the solution for the determination of metals. 6 *M* hydrochloric acid was chosen as the working medium in the following experiment, because the effect of hydrochloric acid concentration on the spectrum was less pronounced.

The detailed conditions for the determination of iron (III) with hydrochloric acid has previously been reported by us<sup>11)</sup> and in this case it was also recommended to measure the absorbance in 6 *M* hydrochloric acid solution.

### Simultaneous Determination of Iron (III), Lead, and Bismuth

In order to determine three elements simultaneously, at least three wave lengths must be selected for the absorbance measurement. In this case four wave lengths were selected: each absorption peak of three elements (Fe: 357 *mμ*, Bi: 327 *mμ*, Pb: 270 *mμ*) and one more wave length of 282 *mμ* at which the absorbance of bismuth is smallest. The calibration curves were made at re-

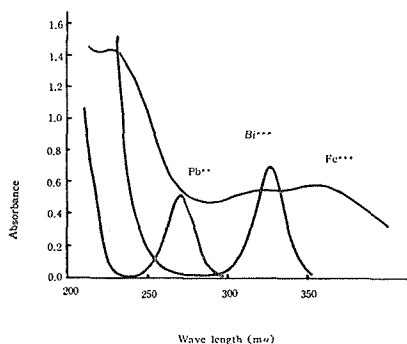


Fig. 3. Absorption spectra of Fe, Pb, Bi in 6*M* HCl. (Concentration of Metal 10.0 p.p.m.).

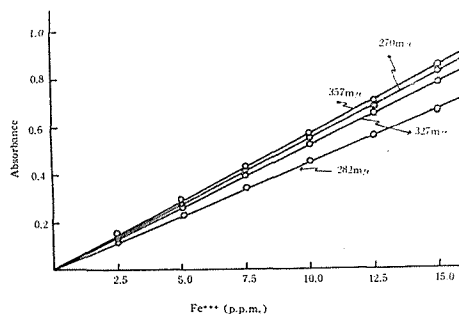


Fig. 4a. Calibration curve.

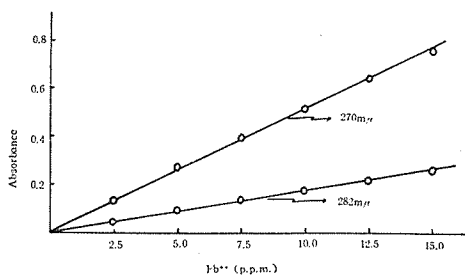


Fig. 4b. Calibration curve.

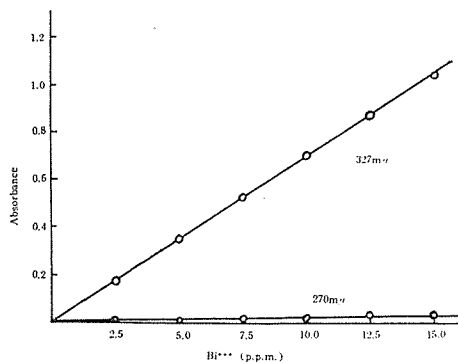


Fig. 4c. Calibration curve.

spective wave length for such concentrations as 2.5, 5.0, 7.5, 10.0 and 15.0 p.p.m. Results are shown in Fig 4. Beer's law is obeyed in all cases. For the purpose of determination of iron, lead, and bismuth each absorbance indexes should be evaluated from the absorbances given in the calibration curves at each of four wave lengths. The absorbance indexes given here are not the molar extinction coefficients but, for convenience in calculation, are arbitrary constants relating the absorbance to the concentration in parts per million at the fixed path length of the cells used in the measurements. These are given in Table 1.

Table 1. Absorbance indexes at various wave lengths.

Wave length (m $\mu$ )	Fe <sup>+++</sup>	Pb <sup>++</sup>	Bi <sup>+++</sup>
270	0.0554	0.0516	0.0017
282	0.0446	0.0173	
327	0.0522		0.0694
357	0.0565		

For the 17 mixed sample solutions in which iron, lead, and bismuth are mixed in various concentration, after measuring the absorbances at the four wave lengths, the amounts of these elements were determined using the absorbance indexes shown in Table 1. The amounts of iron are determined from the absorbance at 357 m $\mu$ . At 327 m $\mu$ , the amounts of bismuth were then calculated from the value which is obtained by subtracting the absorbance corresponding to the amounts of iron from the absorbance measured, and the amounts of lead are obtained at 282 m $\mu$  by the same way. At 270 m $\mu$ , the amounts of lead are able to be calculated by subtracting the absorbance corresponding to the amounts of iron and of bismuth from the absorbance measured. Results obtained are shown in Table 2. From the table, it is observed that the mean error in percent at 282 m $\mu$  is somewhat higher than that of at 270 m $\mu$ . Thus in the simultaneous determination of lead, bismuth, and iron it is most desirable to make the absorbance measurements at each peak of three elements.

Determination of Iron, Lead and Bismuth

Table 2. Simultaneous determination of Fe<sup>+++</sup>, Pb<sup>++</sup>, Bi<sup>+++</sup> by HCl.

Present (p.p.m.)			Fe <sup>+++</sup> Found (p.p.m.) at 357m $\mu$	Bi <sup>+++</sup> Found (p.p.m.) at 327m $\mu$	Pb <sup>++</sup> Found (p.p.m.)	
Fe <sup>+++</sup>	Bi <sup>+++</sup>	Pb <sup>++</sup>			at 282m $\mu$	at 270m $\mu$
2.00	2.00	2.00	2.05	1.97	2.02	1.94
2.00	2.00	5.00	2.02	2.00	4.91	5.02
2.00	5.00	2.00	2.07	5.04	2.08	1.98
5.00	2.00	2.00	5.04	1.94	1.85	1.88
2.00	5.00	5.00	2.04	4.98	4.91	4.97
5.00	2.00	5.00	5.01	1.97	4.68	4.79
5.00	5.00	2.00	5.27	4.95	2.25	2.04
5.00	5.00	5.00	5.10	5.01	4.97	4.85
2.00	5.00	10.00	2.07	4.91	9.88	9.93
2.00	10.00	5.00	2.23	9.92	5.26	4.95
5.00	2.00	10.00	5.03	1.93	9.77	9.87
10.00	2.00	5.00	10.16	2.00	4.86	4.81
10.00	5.00	2.00	10.14	4.98	2.20	1.96
5.00	10.00	2.00	5.19	9.95	2.37	1.98
2.00	2.00	10.00	2.09	1.96	10.29	10.17
2.00	10.00	2.00	2.18	9.86	2.25	1.92
10.00	2.00	2.00	10.14	2.04	2.13	1.98
Mean of error (%)			3.2	1.2	5.7	2.2

**Standard Procedure**

Appropriate aliquots of sample solutions of the elements were taken, to which were added from a pipette 10 ml of concentrated hydrochloric acid, and the whole was diluted with water to 20 ml in a volumetric flask. The absorbance at respective wave length of the maximum for each of the elements was measured. These wave lengths were 357 m $\mu$  for iron, 270 m $\mu$  for lead, and 327 m $\mu$  for bismuth.

**Summary**

In the mixed sample solution of iron, lead, and bismuth, each concentration was calculated in parts per million from the absorbance measurements at the appropriate wave length. All the results of determinations of these elements in various mixed sample solutions were found to be in good agreement with the theoretical value within the error of several percent. The proposed method is simple in operation, convenient in that it has no need of special reagent, and useful in having a sensitivity and an accuracy comparable to those of other common spectrophotometric methods.

The interfering substances in this method will be the same members as in the case of the ultraviolet spectrophotometric determination of iron with hydrochloric acid, as previously reported by us.<sup>11)</sup> The diverse ions such as copper, antimony, vanadium, and titanium will interfere since they give intense absorption in the ultraviolet region under the working conditions. However, these elements can be easily eliminated by appropriate procedure as Merrit described.

The use of the hydrochloric acid is advantageous since it is a more common reagent and lower in cost.

The author wishes to express his sincere appreciation to Prof. Dr. M. Ishibashi for his encouragement and suggestion, and to Mr. K. Hihiro for his earnest assistance throughout the investigation.

REFERENCES

- (1) M. S. Desesa and L. Logers, *Anal. Chim. Acta*, **6**, 534 (1952).
- (2) I. A. Stolyarova, *Zhur. Anal. Khim.*, **8**, 270 (1953).
- (3) W. Nielsch und G. Böltz, *Mikrochim. Acta*, 313 (1954).
- (4) W. Nielsch und G. Böltz, *Anal. Chim. Acta*, **11**, 438 (1954).
- (5) W. Nielsch und G. Böltz, *Z. Anal. Chem.*, **142**, 94, 102, 109 (1954).
- (6) R. Bastian, R. Weberling, F. Pallila, *Anal. Chem.*, **25**, 284 (1954).
- (7) H. L. Greenhouse, A. M. Feiluch and Louis Gorden. *Anal. Chem.*, **29**, 153 (1957).
- (8) R. Bastian, R. Weberling, and F. Pallila, *Anal. Chem.*, **28**, 459 (1956).
- (9) M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi and T. Kitagawa, *Nippon Kagaku Zasshi*, **76**, 758 (1955).
- (10) M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi and T. Kitagawa, *Bull. Chem. Soc. Japan*, **29**, 57 (1956).
- (11) M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi and T. Kitagawa, *Bull. Chem. Soc. Japan*, **30**, 433 (1957).
- (12) M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi and M. Kitayama, *This Bulletin*, **25**, 6, (1957).
- (13) M. Ishibashi, Y. Yamamoto and K. Hihiro, *Japan Analyst*, **7**, 582 (1958).
- (14) M. Ishibashi, Y. Yamamoto and K. Hihiro, under press.
- (15) M. Ishibashi, Y. Yamamoto and K. Hihiro, *This Bulletin*, **36**, 24 (1958).
- (16) C. Merritt, H. M. Hershenson and L. B. Rogers, *Anal. Chem.*, **25**, 572 (1953).