

Spectrographic Determination of Microamounts of Arsenic, Antimony, Bismuth, Tin and Lead

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Spectrographic Determination of Microamounts of Arsenic, Antimony, Bismuth, Tin and Lead*

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Synopsis

After calcium nitrate (used as the spectroscopic buffer) and cadmium nitrate (used as the internal standard) were added to the sample solution, the mixed solution was evaporated and a part of the nitrate salt deposited was excited in the cavity of graphite electrode by direct current arc method with a medium quartz spectrograph. By this salt powder method, at least 3γ of arsenic, 1γ of antimony, 0.3γ of tin and lead, and 0.1γ of bismuth could be determined spectrographically.

I. Introduction

There are many difficulties in determining spectrographically the volatile metals such as arsenic, antimony, bismuth, tin and lead. Especially, the sensitivities of arsenic and antimony, both radiating weak spectral lines, are very low under the usual excitation conditions. Therefore, attempts were first made to extend as low as possible the lower limit of the determination of these metals by a medium quartz spectrograph, and it was seen that calcium was effective as a spectroscopic buffer. After studying other conditions, a spectrographic method was established to determine microamounts of these five elements simultaneously.

II. Experiments and results

1. Apparatus and reagents

The apparatus used was Carl Zeiss Qu 24 spectrograph, and graphite electrodes used (5 mm in diameter) were ones for spectral analysis supplied from the Nippon Carbon Co., in which any lines except those of copper and boron were not detected spectroscopically.

All of solutions of metals were prepared in the form of nitrate. Each solution of arsenic, antimony, bismuth, tin and lead contained 0.1 per cent of each metal and was spectroscopically pure. The solution containing 5 per cent of calcium was not contaminated with arsenic, antimony, bismuth, and tin except iron, aluminium, magnesium and lead, and the quantity of lead was too little to interfere with the determination. The concentration of the solutions containing cadmium, silver, zinc, iron, aluminium, sodium and magnesium were 0.1 per cent as metal, and they were confirmed spectroscopically to be free from arsenic, antimony, bismuth, tin and lead. The other solutions were all free from arsenic, antimony, bismuth, tin and lead.

* The 890th report of the Research Institute for Iron, Steel and Other Metals. Published in Japanese in the Journal of the Chem. Soc. of Japan, **77** (1956), 1668.

2. Preliminary experiments

(i) Spectroscopic buffer

As reported previously⁽¹⁾ the roles of the spectroscopic buffer in arcing are to intensify spectral lines as well as to stabilize arc burning. In order to intensify the spectral lines of the five elements to be determined, several kinds of aqueous solutions of compounds mixed with microamounts of the five elements were excited by arcing after they had been absorbed by electrodes and the change in intensities of the spectral lines was examined. The elements existing in the arc column as the main component show their own arc temperature, and hence four elements from the alkali metal of the lowest arc temperature up to phosphorus of almost the highest arc temperature were chosen: sodium (3700°K), calcium (4300°K), copper (5400°K) and phosphorus (7500°K).⁽²⁾ Thus, the following compounds were chosen as a possible buffer; sodium nitrate, calcium nitrate, cupric nitrate, disodium phosphate and phosphoric acid which were all spectroscopically free from the five elements to be determined. Graphite electrodes used were 25 mm in length, the top being tapered from 2 to 3 mm in diameter. This electrode was prearced by the direct current, giving 5A at 120V, for 30 seconds, and impregnated with 0.1 ml of the following solutions, and then the salt was excited by direct current of 120V, 7A for 10 sec. 6 kinds of the solutions were prepared to contain (1) 1.6 per cent of disodium phosphate, (2) 0.9 N of phosphoric acid, (3) 4.0 per cent of sodium nitrate, (4) 3.0 per cent of cupric nitrate, (5) 4.0 per cent of calcium nitrate, and (6) no buffer, respectively, in addition to 0.03 per cent of arsenic and 0.01 per cent of each of antimony, bismuth, tin and lead. Results of the experiments showed that calcium alone intensified the spectral lines, while the others weakened them. Particularly, cupric nitrate remarkably weakened them. As to the influence of sodium on the line intensities of these metals the same result was shown already.⁽³⁾

In order to investigate quantitatively the influence of calcium, solutions containing 0.003 per cent of each of the five elements and 0, 0.8, 1.6 and 4 per cent of calcium, respectively, were prepared, and after 0.1 ml of the solutions had been absorbed by graphite electrode, they were excited. The solution containing 4 per cent of calcium showed a tendency to diminish the line intensities, which was not measured photometrically. The photometrical results are shown in Table 1, in

Table 1. Influence of calcium on the five elements.
Excitation conditions: DC 120V, 6.3 to 6.5A, exposure of 12 sec.

	As 2349.84Å	Sb 2598.06Å	Bi 3067.72Å	Sn 2839.99Å	Pb 2802.00Å
Ca 1.6 %	1.15	1.63	7.04	3.33	2.04
0.8 "	1.11	1.56	5.02	2.86	1.51
0 "	1.08	1.27	2.37	1.55	1.20
salt powder method	2.3	4.8	14.5	10.9	4.0

(1) Gotô and Yokoyama, J. Chem. Soc. Japan, **75** (1954), 1305; Sci. Rep. RITU, **A8** (1956), 166.

(2) L. H. Ahrens, *Spectrochemical Analysis*, Mass. Addison-Wesley Press (1950), 20.

(3) *ibid*, 208.

which figures are ratios of readings of each spectral line on the scale of microphotometer to that of background. As shown in this table, calcium was proved to be effective on the line intensities of all of the five elements and the effect of calcium on the line intensities of arsenic and antimony was not seen so clearly as in the case of the other three elements, because the spectral lines of arsenic and antimony are weak from the first and blackening of those lines is in the part of the toe of the characteristic curve of photographic plates used.

(ii) Form of sample

In solution method, the graphite electrode can hardly absorb more than 0.1 ml of solution, and so the spectral lines of arsenic and antimony are weak as shown in Table 1. Therefore, the sample solution was evaporated and dried up carefully to deposit calcium nitrate and then it was excited in a crater of electrode. 1 ml of the same solution containing 1.6 per cent of calcium nitrate together with the five elements as used before was evaporated and dried up carefully in a crucible by heating on a hot plate, and after the nitrate salt deposited was sufficiently mixed, about a third of it was excited in a crater (2.5 mm in diameter and 2 mm in depth) of graphite electrode by arcing with a direct current of 120 V and 7.5 A for 15 sec. The result is shown in the lowest line in Table 1. It is possible to consume more than 0.3 ml of solution in an arc burning, if the salt deposited is used for excitation. Consequently, the method was adopted in which the salt deposited was excited after the solution was evaporated.

(iii) Internal standard

It is desirable that the element used as the internal standard should have the volatility similar to that of the five elements, which volatilize easily. Availability of three metals, namely, silver, cadmium and zinc, for the internal standard is examined. Solutions containing all of 0.3 per cent of calcium, 0.0005 per cent of silver, 0.01 per cent of cadmium and 0.025 per cent of zinc together with various amounts of the five elements were prepared, and 1 ml of them was excited by the salt excitation method, and calibration curves were prepared. The results of tin and arsenic are shown in Fig. 1. Calibration curves using silver and cadmium as the internal standard are almost linear, while

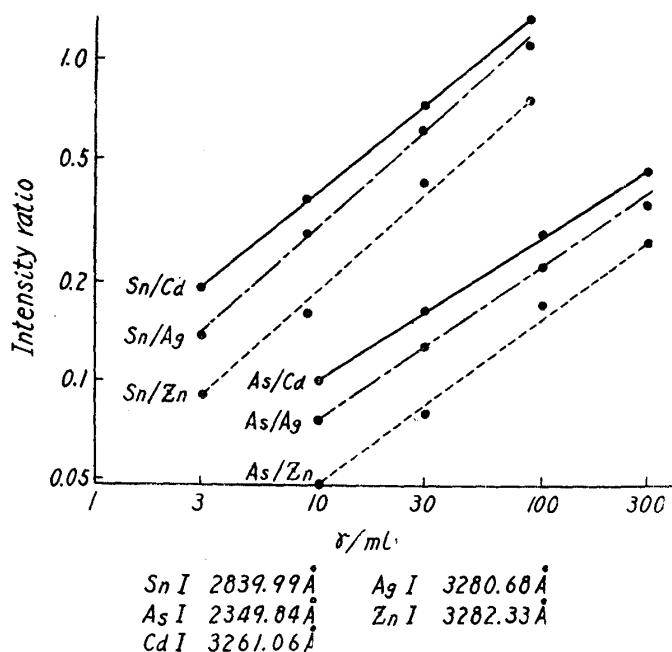


Fig. 1. Working curves where Cd, Ag, and Zn were used as the internal standard, respectively.

zinc used as the internal standard cannot give a good linearity, because it is impossible to use zinc lines of as low exciting potential as in the cases of tin, arsenic and so on. Cadmium gave the best result of the three internal standards.

Next, synthetic sample solution was photographed with the standard solutions, and the concentrations of the five elements were spectrographically determined. The following results were obtained, numerical details being omitted: (i) When the arc gap and the dimensions of the electrodes were not kept strictly constant, the deviations from the true values were large when the silver line was used as the internal standard, whereas good results were obtained by using the cadmium line; (ii) On the contrary, when these excitation conditions were kept constant, the use of the silver line gave nearly as accurate results as in the case of cadmium line.

From the above experiments it was seen that cadmium was the best internal standard, and that silver could be used instead of cadmium, if any sample contained cadmium. The results in the case of cadmium used as the internal standard will be shown.

3. Analytical procedure

(i) Preparation of the standard solutions and sample solutions

The concentration of each element in the standard solutions is shown in Table 2, and these solutions contain 1N of nitric acid. Sample solutions are prepared by adding the calcium nitrate and the cadmium nitrate solution until the concentration of calcium nitrate and that of cadmium nitrate become 3 mg/ml and 0.2 mg/ml, respectively. 1 ml of these solutions are evaporated and dried up carefully in a crucible on a hot plate. The heating must be stopped before the decomposition of nitrate takes place.

Table 2. Concentrations of each element in standard solutions.

	As (γ /ml)	Sb (γ /ml)	Sn (γ /ml)	Pb (γ /ml)	Bi (γ /ml)	Ca (mg/ml)	Cd (mg/ml)
I	9	3	0.9	0.9	0.3	3	0.2
II	30	10	3	3	1	3	0.2
III	90	30	9	9	3	3	0.2
IV	300	100	30	30	10	3	0.2

(ii) Excitation conditions and photographic conditions

Graphite electrode (5 mm in diameter) for spectral analysis supplied from Nippon Carbon Co. was used. The cavity is 1.5 mm in diameter and 2 mm in length and the outer diameter of the top is 3 mm. The outer diameter of the top of counter electrode is 2 mm. The electrodes are prearced by a direct current of 6A for 30 sec. The salts from sample solutions are sufficiently mixed and a third or a fourth of them is placed in the cavities.

Spectrograph:	Carl Zeiss Qu 24 medium quartz spectrograph
Arc gap:	2.5 mm
Intermediate screen:	5 mm

Slit width:	8 μ
Electric source:	Direct current of 120V
Current:	6.0~6.5 A
Exposure:	10 seconds
Photographic plate:	Fuji spectroscopic process type
Development:	FD-31, at 18°C, for 5 minutes, by brushing
Fixation:	FF-1, at 18°C, for 6 minutes
Line pair:	Each of As I 2349.84, Sb I 2598.06, Pb I 2802.00, Sn I 2839.99, and Bi I 3067.72 against Cd I 3261.06

Calibration curves were obtained for each element by measuring the blackening with a microphotometer. The results are shown in Fig. 2, which shows good linearities for all elements.

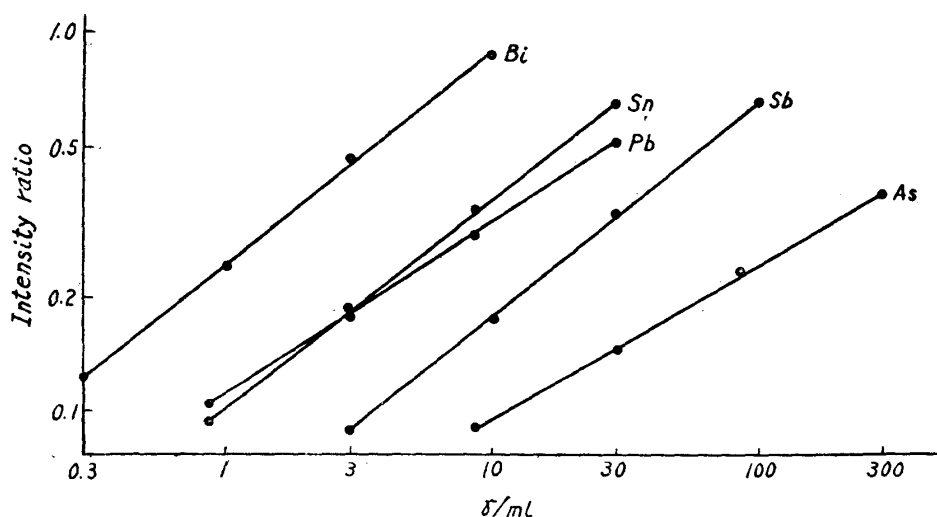


Fig. 2. Working curves

4. Analytical results

A synthetic solution containing the five elements was prepared, treated in the same way as for the standard solutions and photographed on a plate, and then these elements were determined from calibration curves. The results are shown in Table 3, in which relative deviations are 10~11 per cent for antimony, tin and bismuth, 12.5 per cent for arsenic, and 16.1 per cent for lead. Satisfactory results were obtained for the four elements other than lead which showed rather lower precision.

Table 3. Analytical results.

	Added (γ/ml)	Found (γ/ml)					Mean (γ/ml)	Standard deviation in percentage
		60	68	73	77	84		
As	75	60	68	73	77	84	72	12.5
Sb	25	21	23	25	25	28	24	10.7
Sn	7.5	9.0	6.7	8.0	8.0	7.7	7.9	10.4
Pb	7.5	6.0	8.7	7.0	9.0	7.4	7.6	16.1
Bi	2.5	2.5	2.3	2.6	3.0	2.8	2.6	10.2

5. Influences of other substances

Iron, aluminium, sodium, magnesium, sodium phosphate and phosphoric acid were examined for interference in the analysis of the five elements to be determined. The results are shown in Tables 4 and 5. Amounts of elements added were expressed in the weight ratio of the metal added (the elemental phosphorus for the sodium phosphate and the phosphoric acid) to calcium metal. In addition to these, the analytical results in the case of no other substance added are, for comparison, shown in the third column.

Table 4. Influences of other elements (Fe, Al and Na)

Element determined	Added γ /ml	Found γ /ml	Fe (Fe/Ca)			Al (Al/Ca)			Na (Na/Ca)		
			1/10	1/2	2	1/50	1/10	1/2	1/50	1/10	1/2
As	45	46	48	46	64	36	52	48	48	44	50
Sb	15	16.0	24.6	—	—	15	18	16.6	16.4	15.0	15.6
(Sb)	15	15.6	16.4	17	17	—	—	—	—	—	—
Pb	4.5	4.3	4.8	5.0	—	3.6	3.2	5.0	4.8	4.6	5.2
Sn	4.5	4.9	4.2	4.6	—	5.6	5.6	5.0	4.6	5.0	4.2
Bi	1.5	1.4 ₆	3.2	—	—	1.5 ₄	1.8 ₄	1.7 ₀	1.3 ₆	1.3 ₈	1.3 ₄

Table 5. Influences of other elements (Mg and P)

Element determined	Added γ /ml	Found γ /ml	Mg (Mg/Ca)			Na ₂ HPO ₄ (P/Ca)			H ₃ PO ₄ (P/Ca)		
			1/30	1/10	1/2	1/30	1/10	1/3	1/30	1/10	1/3
As	75	80	76	85	88	73	50	39	93	120	160
Sb	25	25.5	28	28	27	—	—	—	—	—	—
Pb	7.5	7.5	7.9	6.8	4.7	4.4	6.5	10.5	8.8	13.5	5.5
Sn	7.5	7.3	7.5	6.8	5.6	11.5	11.2	11.7	7.0	5.9	3.5
Bi	2.5	2.6 ₅	2.7 ₅	2.2	2.0 ₅	2.4	2.0	1.7 ₂	2.4	2.8	2.1

Iron: When the ratio Fe/Ca is greater than 1/10, Fe 2598.37 and Fe 3067.24 adjacent to Sb I 2598.06 and Bi I 3067.72, respectively, interfere for their duplication. Antimony was determined successfully by substituting Sb I 2311.47 (it is comparatively strong and represented by (Sb) in Table 4) for Sb I 2598.06. As for bismuth, another suitable line could not be found. As the ratio Fe/Ca became greater than 1/2, ferric oxide in the matrix was excessive, volatilization of the sample was very rapid, spectral lines became remarkably strong and, therefore, the difference in the compositions between the standards and the sample was clearly recognized. The analytical results for the ratio Fe/Ca of 1/2 and 2 in Table 4 are obtained by using the standards containing the same amount of iron as that in the synthetic sample. Thus, it is possible to determine arsenic, antimony, tin and lead, if the ratio Fe/Ca is less than 1/2.

Aluminium: Aluminium suppressed the volatilization of the other coexisting elements and weakened noticeably the spectral line of cadmium as well as those of the five elements. The standards with the same concentration of aluminium as that of the synthetic sample were used for the ratio Al/Ca of 1/2 in the table; nevertheless satisfactory results were not obtained. Consequently, aluminium should

be removed before the spectral analysis.

Sodium: Similarly to the results of the preliminary experiments, this metal weakened the spectral lines of the five elements and also that of cadmium to the same extent as for the former. As shown in the table, therefore, the determination is able to be done in presence of sodium up to $1/10 \sim 1/2$ of the ratio Na/Ca.

Magnesium: The elements are mostly able to be determined up to $1/30 \sim 1/10$ of the ratio Mg/Ca.

Disodium phosphate and phosphoric acid: Both suppressed the volatilization of the other elements and made the arc unstable. Therefore, they must not coexist.

Summary

(1) The spectrographic method was studied to determine microamounts of the five elements, arsenic, antimony, bismuth, tin and lead, simultaneously.

(2) It was seen that in the arcing of the five elements calcium stabilized the arc and intensified the spectral lines. Therefore, in this method calcium was added to the sample as the matrix, and the nitrate salt powder was excited by arcing.

(3) Silver and cadmium were suitable for the internal standard and, especially, the latter gave good results.

(4) This method is available for above 3γ of arsenic, above 1γ of antimony, above 0.3γ of tin and lead and above 0.1γ of bismuth. The relative deviations were $10 \sim 16$ per cent.

Acknowledgement

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