

Precision on the Determination of Trace Elements in Coal

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1 Introduction

The quantity of mineral matter contained in coal is generally 5 to 25 per cent of the total contents. Most of the mineral matter are contained in the form of silicate, while the rest of a few per cent are trace elements with more than 20 kinds including zinc, cadmium, lead, nickel, chromium, copper, and vanadium etc..

At the present moment, it would not be so important to find out the quantity of these trace elements in coal for the purpose of recovering raw materials except certain materials such as germanium and gold, however to know the quantity of trace elements in coal is becoming more important for the purpose of the environmental chemistry.

There are following problems in conducting the determination of trace elements;

- 1) Concentration of the elements are slight.
- 2) Coal is composed of organic matter.
- 3) Difficulty in obtaining a standard sample required for the determination.

To cope with these problems, the Sample Research Committee, JUSE, has conducted a Round-Robin study with cooperation of seven laboratories and tried to evaluate the precision of the determination of trace elements in coal and coke. Besides, it was considered that volatility loss at the stage of pretreatment of sample might have occurred for the elements with inferior reproducibility such as zinc.

The result of the study is described hereinafter.

2 Experimental

2-1 Design of Experiment

Three kind of test samples crushed under 250 μ m, shown in Table 1, were analyzed at seven laboratories by the analytical method described below. Each kind of sample was analyzed two times and the measurement by the atomic absorption method was performed twice respectively.

Analytical procedure was as follows;

Transfer 1g of the sample, weighed to the nearest 0.1mg, to a platinum dish. Add 5ml of HF and 10ml of HNO₃. Evaporate to white fumes to expel all HF. Transfer the sample to 200ml beaker, add 30ml of HNO₃, and 10ml of HClO₄. Cover the beaker, and heat until the solution becomes clear. Evaporate to dense white fumes. Cool, and approximately 50ml of water. Filter through a texture paper, and wash the residue with warm HCl (2+100). Transfer the residue to a platinum crucible, ignite, fuse with 2g of Na₂S₂O₇, and then add to the original solution. Transfer to a 100ml volumetric flask, and dilute exactly to the mark with water. Measure the absorption of an aliquat by an atomic absorption apparatus.

2-2 Result of Experiment

Original data obtained are shown in Table 2. About 600 data obtained are statistically analyzed, and the precision calculated by using ANOVA (nested design) are summarized in Fig. 1, Fig. 2, and Fig. 3 respectively. (See formulas (1), (2)

and (3)).

Repeatability (Error due to A.A. method only),

$$\sigma_E = \sqrt{v_E}, \quad \text{C.V. } \sigma_E = \sigma_E / \bar{x} \times 100 \quad \dots\dots\dots (1)$$

Repeatability (Error due to pretreatment),

$$\sigma_P = \sqrt{(v_L - v_P) / 4}, \quad \text{C.V. } \sigma_P = \sigma_P / \bar{x} \times 100 \quad \dots\dots\dots (2)$$

Reproducibility (Error among different laboratories),

$$\sigma_{\bar{x}} = \sqrt{\sigma_L^2 + \sigma_E^2 / 2 + \sigma_P^2 / 2}, \quad \text{C.V. } \sigma_{\bar{x}} = \sigma_{\bar{x}} / \bar{x} \times 100 \quad \dots (3)$$

2-3 Discussion

2-3-1 Repeatability within same laboratory

As is evident from Fig. 3, C.V. of repeatabilities (C.V. σ_E) are less than 10% except cadmium and lead. These inferior repeatability of the above two elements may be due to the contents of them closing to the detection limit of the A.A. method as shown in Table 3.(1) In such a case, pre-extraction procedure may be effective to improve the precision.(2)

2-3-2 Error due to pretreatment

As is evident from Fig. 1, C.V. of pretreatment (C.V. σ_P) for zinc is inferior than that of other elements. It suggests that volatility loss of zinc may be occurred during decomposition.

The supplemental experiment using seven samples, therefore, has been carried out to study the effect of pretreatment for the determination of zinc. The following three pretreatments have been compared on the zinc. In addition, nickel has also been determined from the same solution as a reference, because it has higher boiling point than that of zinc.

- 1) Low temperature ashing method.
- 2) High temperature ashing method.
- 3) Wet oxidation method employed on the above Round-Robin Study.

As is evident from Fig. 4 showing the effect of pretreatments, significant loss during incineration was observed technically compared to the wet oxidation method in case of zinc. On the other hand, no significant bias was observed among the three methods in case of nickel. Anyway, the volatility loss of zinc during pretreatment should be studied more precisely because it may results the inferior precision.

2-3-3 Reproducibility between different laboratories

As is evident from Fig. 2, the C.V. of reproducibilities (C.V. $\sigma_{\bar{x}}$) calculated using all of the data including outliers, were almost more than 20%. Even if the outliers are excluded, most of the elements still show inferior reproducibility.

3 Conclusion

- 1) The precisions (repeatability and reproducibility) on the determination of trace elements in coal and coke (zinc, nickel, chromium, copper, lead, cadmium, and vanadium) are insufficient on the viewpoint of coefficient of variance ($\sigma_x / \bar{x} \times 100$) on the most elements are more than 20% when outliers are not rejected.
- 2) C.V. of cadmium and lead are inferior because of substantial difficulties on the

A.A.method. That is, the contents of cadmium are close to the detection limit, and the lack of sensitivity for the determination of lead may cause these inferior precision respectively.

- 3) In case of the determination of zinc, the more precise studies on the pre-treatment should be carried out in the future.

Afterwords

These studies were carried out in Japan prior to the first international Round-Robin Study of ISO/TC 27/WG 14 (Trace elements). A part of the statistical analysis on the above experiment was reported in a document ISO/TC 27/WG 14, No. 6 (Japan-6).

Literature cited

- (1) "Atomic Absorption Spectrophotometry in the Steel Industry", The Iron and Steel Institute of Japan, (1975) P. 52 - P. 53.
- (2) "Round-Robin Studies for the Estimation of Accuracy and Precision of Pollution and Environment Control Analysis", The fourth SAC Conference (1977).

Table 1 Proximate Analysis of the Samples

% of the Air-Dried Coal and Coke

Samples	Moisture	Ash	*V.M.	**F.C.
U.S. Massey H.V. Coal	1.4	13.2	32.4	52.6
Japanese Miike Coal	9.9	6.5	38.3	54.2
Metallurgical Coke	0.1	11.6	0.5	87.8

* Volatile Matter ** Fixed Carbon

Table 2 Trace Elements in Coal and Coke

PPM in Air-Dried Whole Coal and Coke

(1) Sample ; U.S. Massey H.V. Coal

Lab.	Zn		Cd		Pb		Ni		Cr		Cu		V		
	P ₁	P ₂													
A	m ₁	29.0	17.2	0.26	0.26	5.15	3.83	11.2	11.9	15.2	17.2	16.9	16.5	34.3	30.4
	m ₂	27.7	17.2	0.13	0.26	6.47	5.15	10.6	10.6	17.2	17.2	15.3	15.3	29.0	27.1
B	m ₁	27.1	26.0	0.34	0.45	8.58	8.32	12.5	12.5	20.5	19.4	17.2	19.3	32.1	30.8
	m ₂	27.3	26.4	0.34	0.43	8.05	8.05	12.5	12.5	20.7	19.4	17.2	18.3	32.1	30.8
C	m ₁	11.6	23.0	<u>0.95</u>	<u>2.09</u>	4.22	0.26	18.6	12.7	14.7	22.7	16.6	26.6	30.6	33.4
	m ₂	12.0	20.7	<u>0.66</u>	<u>1.25</u>	5.15	8.18	9.6	12.4	19.5	23.4	17.2	14.5	23.2	26.0
D	m ₁	16.9	22.0	0.95	0.40	7.52	7.26	12.3	12.3	19.7	19.7	20.5	20.5	32.7	31.9
	m ₂	17.0	20.7	0.75	0.63	11.9	9.50	15.0	13.2	16.5	16.9	19.8	20.7	30.6	30.5
E	m ₁	23.9	18.6	0.48	0	10.6	11.9	<u>20.6</u>	<u>20.9</u>	<u>7.5</u>	<u>8.6</u>	21.6	23.5	25.2	28.1
	m ₂	21.6	18.6	0.48	0	10.6	11.9	<u>20.6</u>	<u>20.9</u>	<u>7.7</u>	<u>8.3</u>	20.9	21.9	25.2	29.1
F	m ₁	19.7	12.2	0.21	0.21	5.15	4.49	10.4	10.0	21.3	19.1	17.4	18.2	29.6	26.4
	m ₂	18.7	22.0	0.17	0.17	5.02	4.49	10.3	9.8	21.3	19.3	17.4	18.2	28.5	26.4
G	m ₁	21.8	18.1	0.32	0.18	3.34	5.41	11.9	11.5	17.7	18.9	19.0	16.8	31.2	31.9
	m ₂	21.6	18.2	0.26	0.22	2.38	5.68	12.1	11.7	17.4	18.5	18.5	16.4	31.2	31.7

p ; pretreatment , m ; measurement

— Outliers

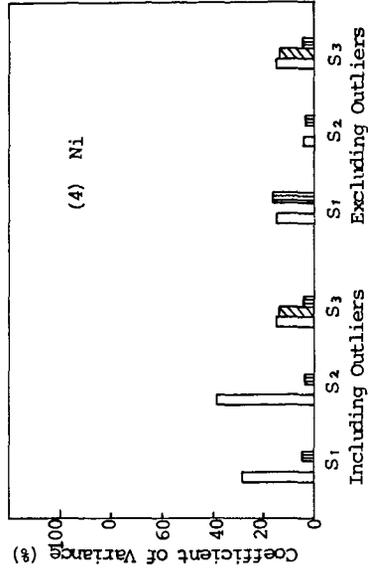
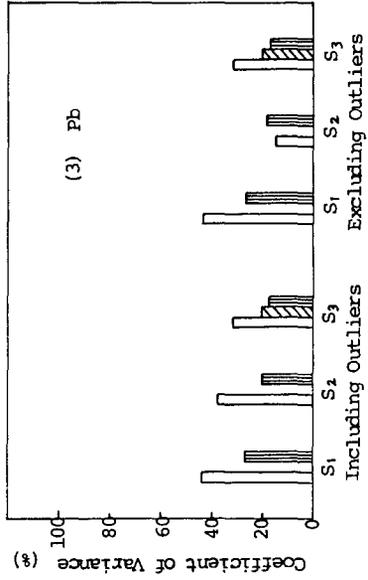
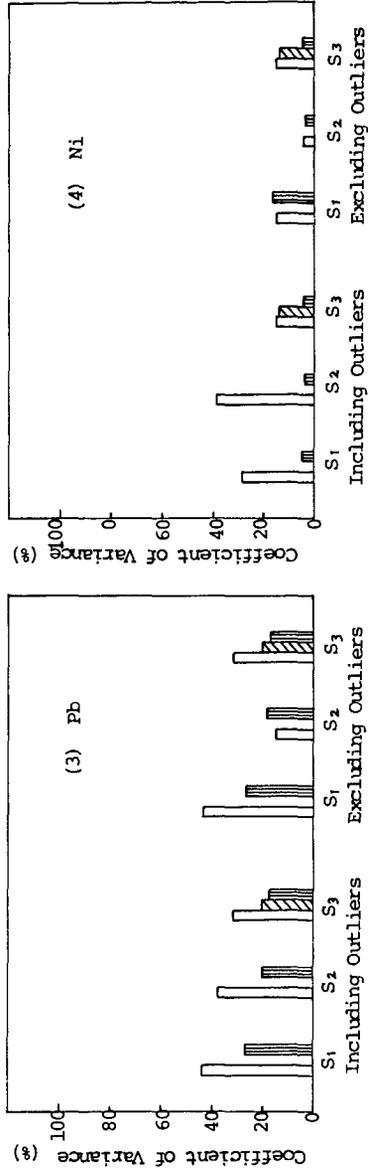
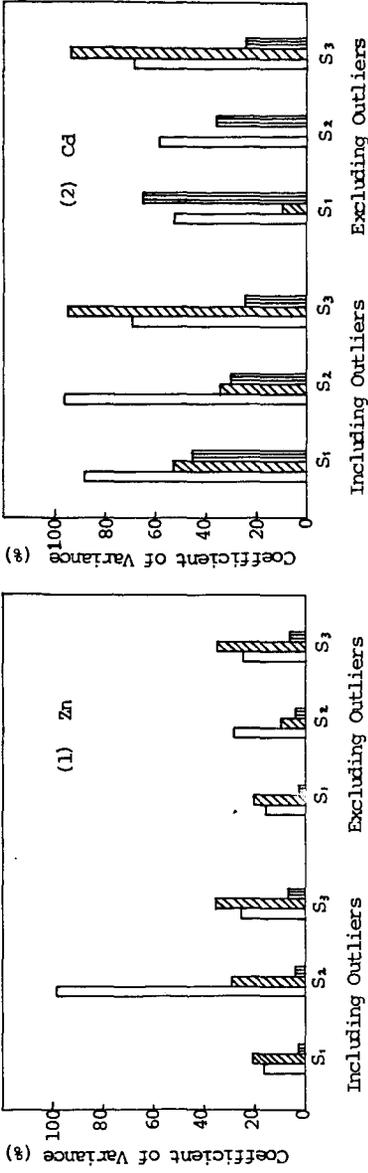
Table 2 Concluded

(2) Sample ; Japanese Miike Coal

Lab.	Zn		Cd		Pb		Ni		Cr		Cu		V	
	P ₁	P ₂	P ₁	P ₂	P ₁	P ₂	P ₁	P ₂	P ₁	P ₂	P ₁	P ₂	P ₁	P ₂
A	m ₁	3.58 3.90	0.13 0.13	3.19 1.89	18.9 18.5	8.45 8.45	5.72 5.59	<u>4.55</u> <u>4.55</u>						
	m ₂	2.93 3.58	0.07 0	3.19 3.19	18.5 18.5	8.45 8.45	5.07 5.07	<u>4.55</u> <u>4.55</u>						
B	m ₁	<u>27.0</u> <u>26.7</u>	0.20 0.21	2.99 3.51	20.3 20.6	10.4 9.62	6.24 6.50	7.15 7.15						
	m ₂	<u>27.1</u> <u>26.8</u>	0.20 0.21	3.06 3.45	20.2 20.5	10.4 9.55	6.24 6.31	7.22 7.02						
C	m ₁	<u>35.4</u> <u>21.5</u>	<u>0.56</u> <u>0.81</u>	3.25 3.45	49.4 7.5	8.13 11.0	5.59 5.46	4.62 6.96						
	m ₂	<u>23.8</u> <u>23.1</u>	<u>0.39</u> <u>0.73</u>	2.21 1.56	22.8 13.0	9.75 11.4	5.72 6.24	4.75 10.9						
D	m ₁	4.29 4.36	0.18 0.20	<u>4.42</u> <u>4.03</u>	19.9 19.8	9.43 10.9	6.50 6.63	5.92 6.57						
	m ₂	4.42 4.36	0.31 0.34	<u>5.33</u> <u>5.33</u>	22.1 21.4	8.84 9.10	6.37 6.37	4.75 5.92						
E	m ₁	5.20 4.10	0.12 0.12	3.90 3.25	25.3 23.7	<u>2.86</u> <u>2.86</u>	6.70 6.70	4.68 8.00						
	m ₂	4.75 4.23	0.12 0.12	3.90 3.25	25.3 25.3	<u>2.86</u> <u>2.86</u>	6.70 6.63	8.00 4.86						
F	m ₁	4.55 4.42	0.07 0.07	3.25 2.80	19.3 19.0	9.62 10.7	5.59 5.72	<u>4.23</u> <u>4.23</u>						
	m ₂	4.55 4.36	0.07 0.07	3.38 2.80	19.2 19.2	9.69 10.5	5.66 5.86	<u>4.42</u> <u>4.23</u>						
G	m ₁	9.00 6.50	0.10 0.10	<u>0.78</u> <u>1.56</u>	13.7 14.0	9.62 9.69	5.66 6.11	5.98 6.50						
	m ₂	7.67 6.50	0.11 0.11	<u>1.56</u> <u>1.76</u>	14.0 13.3	8.71 8.58	8.85 6.11	5.98 6.50						

(3) Sample ; Metallurgical Coke

Lab.	Zn		Cd		Pb		Ni		Cr		Cu		V	
	P ₁	P ₂												
A	m ₁	24.4 14.5	0.23 1.16	4.52 5.68	41.8 43.5	22.6 19.1	24.4 24.4	47.6 46.4						
	m ₂	24.4 13.3	0 1.16	6.73 7.89	40.6 42.3	22.6 20.9	21.8 22.9	55.1 51.0						
B	m ₁	16.2 16.0	0.25 0.34	5.92 6.38	44.7 44.7	24.9 24.0	24.9 25.8	55.3 54.9						
	m ₂	16.2 16.2	0.24 0.34	6.03 6.38	44.4 45.2	25.1 24.0	24.9 25.8	55.1 54.3						
C	m ₁	10.2 12.1	0.37 1.30	4.41 2.20	78.3 7.0	19.7 34.8	24.2 21.5	30.2 45.8						
	m ₂	10.3 17.6	0.41 1.31	6.73 4.87	41.8 23.2	20.3 24.4	24.8 24.0	36.0 48.7						
D	m ₁	15.2 13.5	0.43 0.38	9.05 9.63	44.3 44.3	22.9 21.9	26.8 26.9	56.0 53.2						
	m ₂	14.6 13.9	0.58 0.57	10.4 8.70	50.6 50.2	18.7 21.7	25.8 25.8	55.3 55.0						
E	m ₁	16.7 15.3	0.42 0	9.28 5.92	48.4 50.7	7.5 7.5	28.8 28.8	41.8 42.8						
	m ₂	16.1 15.3	0.42 0.21	6.96 5.92	51.2 54.8	7.5 7.5	28.8 29.0	33.4 34.1						
F	m ₁	14.0 13.9	0.14 0.14	4.99 4.64	47.8 71.3	27.8 25.3	25.9 25.3	50.8 51.3						
	m ₂	14.0 13.9	0.21 0.21	4.99 4.87	48.0 71.6	27.5 24.9	25.9 25.5	49.9 52.0						
G	m ₁	15.3 15.5	0.17 0.21	6.26 2.09	39.9 40.4	23.3 23.9	24.8 24.1	61.2 49.2						
	m ₂	15.5 15.1	0.15 0.19	5.92 1.74	39.4 39.4	23.0 23.9	26.4 26.0	55.2 58.0						



□ Repeatability C.V. σ_r , ▨ Repeatability C.V. σ_p , ▩ Repeatability C.V. σ_w
 Sample : S₁; U.S. Massey H.V. Coal, S₂; Japanese Miike Coal, S₃; Metallurgical Coke

Fig. 1 Precision on the Determination of Trace Elements

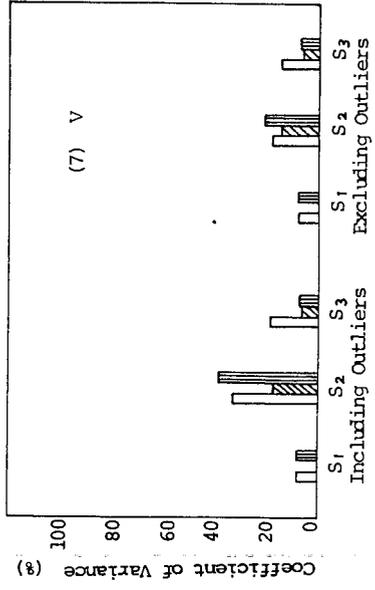
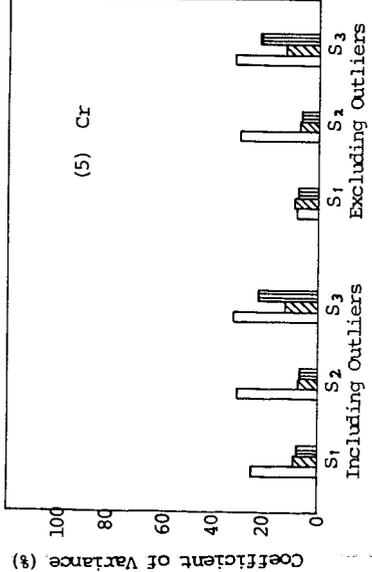
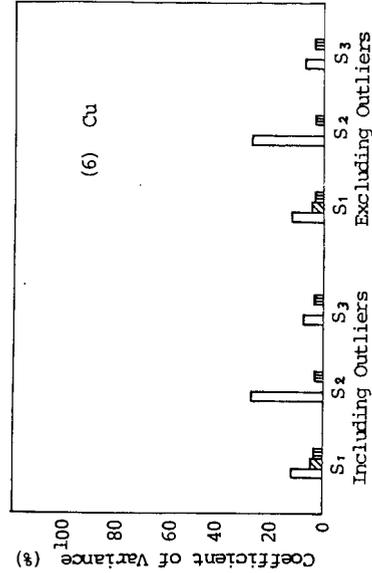


Fig. 1 Concluded

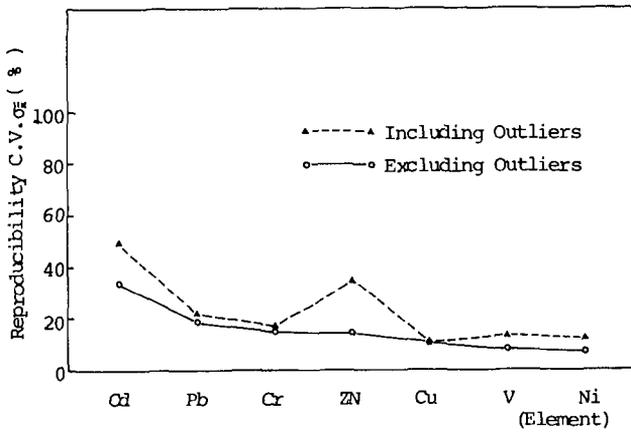


Fig. 2 Error among Different Laboratories

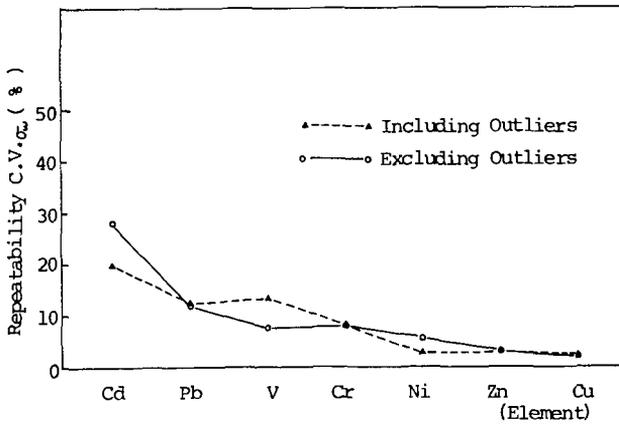
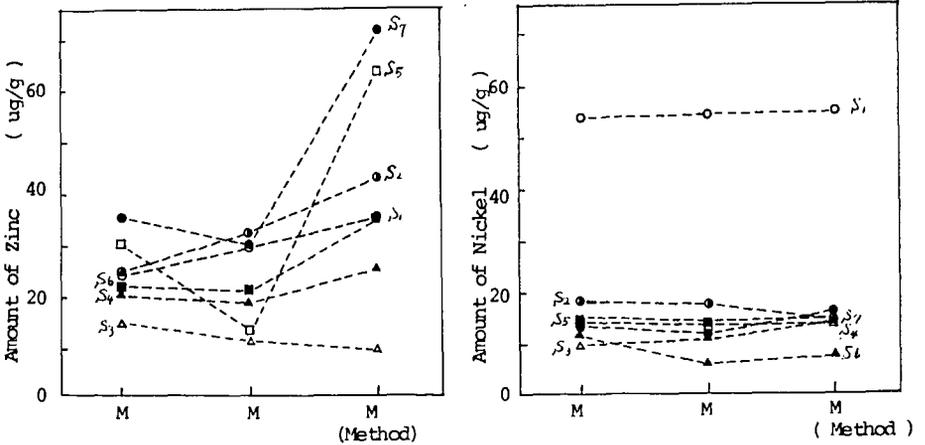


Fig. 3 Error due to Atomic Absorption Analysis

Table 3 Detection Limit and Sensitivity of the Atomic Absorption Method

Element	Line Å	Detection Limit µg/ml	Sensitivity 1% Absorption µg/ml	Analytical Rang of Sample µg/ml
Zn	2138	0.02	0.04	0.1~0.2
Cd	2288	0.002	0.02	0.02~0.04
Pb	2833	0.03	0.5	0.03~0.07
Ni	2320	0.005	0.1	0.06~0.2
Cr	3579	0.003	0.08	0.03~0.2
Cu	3247	0.005	0.1	0.06~0.2
V	3514	0.04	1.3	0.06~0.3



M₁: Low temperature ashing method, M₂: High temperature ashing method
M₃: Wet oxidation method
S₁: Metallurgical coke, S₂: Hongei coal, S₃: Beatrice coal, S₄: Vicary coal
S₅: Pittoston coal, S₆: Black water coal, S₇: Yutoku coal

Fig. 4 Comparison of Analytical Values of Zinc and Nickel in Coal and Coke by Three Decomposition Method