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A STUDY ON KOREAN ANTHRACITE BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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Abstract : By the instrumental neutron activation analysis using two comparators of gold and cobalt, 31 elements have been anlalyzed in anthracites collected from two main coal-fields in Korea. The average concentrations and ranges of the elements were obtained with the elemental difference between two coal-fields. The trends of rare-earth elemental distribution and vertical elemental distribution are also given.

요약 : 2개 광산의 무연탄을 Co와 Au 비교체를 사용한 비파괴 중성자 방사화분석법으로 분석하여 31개 원소들의 함량을 구했다. 각 원소의 평균 함량과 함량 범위를, 그리고 광산의 원소별 함량 차이를 제시하였다. 또한 희토류원소들의 원자량에 따른 함량 분포의 경향과 광상의 깊이에 따른 원소들의 함량 변화를 제시하였다.

Key words : anthracite, INAA, REE distribution

INTRODUCTION

Although the consumption of coal has been decreased, the coal is still one of the most important fuels in Korea and its consumption is larger than one third of total consumption of fuels. Most of the coal produced in Korea is anthracite. The anthracite coal-fields of Korea are confined to areas where sedimentary rocks of Permian and Jurassic geological periods have been preserved.

As coal contains many trace elements, coal combustion and coal conversion are at present under scrutiny as potential sources of pollution. It is important to prepare reliable analytical methods which can monitor the inorganic constituents in coal at various stages of production and utilization. Practically all available analytical methods have been utilized for the characterization of coal. Several representative analytical methods are atomic spectroscopy, spark source mass spectrometry, X-ray fluorescence and neutron activation analysis.[1]

Neutron activation analysis, in particular, has been extensively utilized due to its ability for simultaneous multi-elemental determination. Since most instrumental neutron activation analysis methods do not need sample decomposition, this is a particularly attractive feature in coal analysis due to the difficulties encountered in dissolving this material without significant loss of some elements.

In this work, anthracites collected from two main anthracite coal fields have been analyzed by the instrumental neutron activation analysis method using two comparators of gold and cobalt,[2] to present the average concentrations and ranges of trace elements. In addition, the characteristics of anthracites have been surveyed with the environmental circumstance of their coal-fields.

EXPERIMENTAL

Five anthracite samples were collected from five seams of Samcheok coal-field, which evolved at permian geological period in pelagic environmental circumstance and locates at the Eastern part of Korean peninsula, and 12 anthracite samples were collected from 30 seams of Chungnam coal-field, which evolved at Jurassic period in lacustrine environmental circumstance and locates at Western part of Korean peninsula. These 17 samples were ground into fine powder. A moisture determination was performed by drying samples overnight at 150℃.

Each sample was weighed out 100mg and put into a pre-decontaminated silica ampoule. The ampoule was irradiated at the rotary specimen rack of TRIGA Mark Ⅲ reactor for 20 h with two comparators of gold and cobalt. The two comparators were an alloy of gold-aluminum(0.1274% of gold, Degussa, FRG) and an alloy of cobalt-aluminum(0.0925% of cobalt, Degussa), respectively. The irradiated sample was transferred into a polyethylene vial.

After 4 d cooling, the activity of the sample was counted by a 70cc HPGe detector(FWHM at 1.332 MeV of Co-60=1.9 KeV, CANBERRA, U. S. A.) coupled with 4096 channel analyzer(S-90, CANBERRA)for measuring medium-lived nuclides. The counting time was 600 s. The 10 nuclides of Sm-153, Np-239(U), Br-82, As-76, W-187, Ga-72, Na-24, K-42, Pr-142 and La-140 were observed in the gamma-ray spectrum. The activity was counted again for measuring long-lived nuclides after one month cooling. In this case, counting time was 2,000 s. The 21 nuclides of Ce-141, Yb-169, Lu-177, Se-75, Pa-233(Th), Cr-51, Ba-131, Hf-181, Sr-85, Nd-147, Zr-95, Cs-134, Tb-160, Sc-46, Rb-86, Fe-59, Zn-65, Ta-182, Co-60, Eu-152 and Sb-124 were observed in the spectrum.

The peak identification and activity determination of each nuclide in the above two spectra were done by the program PIAD(Peak Identification and Activity Determination)[3], which had been developed to complement the peak identification procedure in SAMPO-80. However, the procedure of activity determination is similar to this. The radionuclides selected in this work are shown in *Table* 1 with related data. The content of each element was calculated by the single comparator method using two comparators of gold and cobalt. The analysis was repeated 5 times and the results agreed with each other within 10% deviation.

RESULTS AND DISCUSSION

A summary of the average of 31 elemental composition of the anthracites collected from two main coal-fields in Korea, Chungnam and Samcheok, is shown in *Table* 2. The ranges in concentration of the elements noted in this table were observed in the set of 12 anthracites from Chungnam coal-field and in the set of 5 anthracites from Samcheok coal-field. These ranges are similar with those of other countries[4~7], but higher for W, K, La, Th and Rb in Chungnam anthracites.

Compared to Samcheok anthracites, Concentrations of Chungnam anthracites tend to be greater in many elements such as Sm, Br, As, W, Na, K, Pr, La, Ce, Th, Cr, Ba, Hf, Nd, Zr, Cs, Rb, Ta, Co, Eu and Sb. They are similar in contents of U, Ga, Yb, Lu, Tb and Sc, and lower in Se, Sr, Fe and Zn. Especially, in Na, K, Th, Cr, Ba, Rb and Ta, they are

Table 1. Nuclear Characteristics of the Elements Determined by INAA

Element	Target nuclide	Isotopic abundance	Thermal neutron cross-section(barn)	Half-life	γ-ray energy (KeV)
Sm	Sm-152	0.266	206	1.95d	103.2
U	U-238	0.992746	2.68	2.346d	277.6
Br	Br-81	0.4931	2.7	1.473d	554.3
As	As-75	1.0	4.5	1.097d	559.1
W	W-186	0.2864	37.9	28.85h	685.8
Ga	Ga-71	0.399	4.71	14.12h	834.0
Na	Na-23	1.0	0.53	15.03h	1368.6
K	K-41	0.0673	1.46	12.361h	1524.6
Pr	Pr-141	1.0	11.5	19.2h	1575.6
La	La-139	0.9991	8.93	1.678d	1596.5
Ce	Ce-140	0.8848	0.57	32.55d	145.4
Yb	Yb-168	0.00127	2300	32.02d	198.0
Lu	Lu-176	0.0259	2090	6.71d	208.4
Se	Se-74	0.009	51.8	118.45d	264.7
Th	Th-232	1.0	7.37	26.96d	311.9
Cr	Cr-50	0.0435	15.9	27.701d	320.0
Ba	Ba-130	0.00106	11.3	12d	373.2
Hf	Hf-180	0.3522	13.04	45.45d	482.0
Sr	Sr-84	0.0056	0.87	64.85d	514.0
Nd	Nd-146	0.1719	1.4	10.982d	531.0
Zr	Zr-94	0.1728	0.0499	63.98d	756.7
Cs	Cs-133	1.0	29.0	2.062y	795.8
Tb	Tb-159	1.0	23.4	72.1d	879.4
Sc	Sc-45	1.0	27.2	83.8d	889.3
Rb	Rb-85	0.7217	0.48	18.82d	1077.2
Fe	Fe-58	0.0028	1.28	44.56d	1099.2
Zn	Zn-64	0.486	0.76	244d	1115.5
Ta	Ta-181	0.99988	20.5	115d	1189.0
Co	Co-59	1.0	37.18	5.272y	1332.5
Eu	Eu-151	0.4786	5904	13.2y	1408.1
Sb	Sb-123	0.427	4.15	60.2d	1691.0

3 times greater than those of Samcheok anthracites. This variation of the concentrations of the elements should be due to the fact that the anthracite samples were taken from the fields which evolved at different geological periods(Jurassic and Permian periods) and under the different environmental circumstances(lacustrine and pelagic environments), and that the chemical compositions of local earth crust and of the plants that once lived there were different.

Nine rare-earth elements of Sm, Pr, La, Ce, Yb, Lu, Nd, Tb and Eu have been determined. The ratio of the concentrations of rare-earth elements in two kinds of anthracites is plotted along with their atomic numbers in *Fig*. 1. As shown in *Fig*. 1, The minimum value is 0.33 for La, which is the most light one among the rare-earth elements analyzed in this experiment, and the maximum value is 1.3 for Lu, which is the heaviest one. This ratio increases as the atomic number increases. The-

Table 2. Analytical Results of Korean Anthracites and the Comparison with the Contents of Other Countries' (ppm)

Element	Chung-nam		Sam-cheok		China[4]	U. S. A[5]	Japan[6]	Australia[6]	Turkey[7]
	mean	range	mean	range	range	range	range	range	range
Sm	6.28±3.9	0.98~43.33	3.56±2.29	1.0~6.88	0.08~14.4	0.5~3	1.43~6.1	1.87~4.3	0.42~1.52
U	1.77±1.0	0.27~4.01	2.23±1.26	0.9~3.59	0.16~21	0.5~3	0.64~1.1	0.84~1.76	0.19~3.31
Br	6.34±3.6	0.67~15.17	2.20±1.3	1.17~4.37	0.12~46.9	0.5~50	1.26~8.8	1.05~89	1.04~13.5
As	2282±17.33	0.48~53.14	13.49±9.51	1.3~29.63	0.32~120	0.5~100	2.6~4.0	1.52~4.0	10.66~343.9
W	8.24±5.18	0.77~15.34	2.64±1.89	0.76~5.76	0.22~30.7	0.3~1	0.43~1.03	0.43~1.24	–
Ga	41.93±35.58	11.21~121.8	40.5±35.35	10.24~90.82	–	–	–	–	–
Na	3118±3423	323.1~11330	710.0±396.9	340.9~1348	18.5~4600	200~4000	1470~4400	121~1050	93.8~5165
K	56250±34250	17150~116300	5323±5612	513.2~14060	99.4~13000	200~4000	1250~4200	650~3400	40~1400
Pr	20.21±14.75	5.2~39.82	8.6±5.27	1.54~17.02	–	–	<4.5~5.3	2.9~3.2	–
La	60.5±33.08	15.74~120.0	19.71±18.83	2.29~51.56	0.58~91.6	4~20	4.7~10.4	5.7~12.5	1.17~12.7
Ce	45.68±22.88	11.59~85.5	17.67±16.87	2.7~45.92	3.43~183	7~40	12.0~19.4	14.2~28	0.92~9.49
Yb	1.53±0.6	0.44~2.36	1.55±1.01	0.4~3.06	0.05~6.19	0.3~1.8	0.67~1.59	1.11~2.6	0.58~8.44
Lu	0.24±0.09	0.06~0.35	0.28±0.18	0.07~0.54	0.01~1.04	0.04~0.2	0.12~0.29	0.19~0.39	0.01~0.15
Se	0.68±0.46	0.17~1.56	1.1±1.04	0.12~2.77	0.05~12.5	0.5~10	<0.3~0.75	<0.3~0.71	0.82~3.12
Th	21.87±13.86	4.9~40.66	3.18±2.46	0.52~6.19	0.09~25.4	1~6	1.98~4.0	2.7~6.0	0.29~8.46
Cr	35.28±14.69	14.36~62.64	6.94±5.1	1.47~15.21	0.46~125	4~10	9.1~26	5.4~30	9.84~543.7
Ba	193.7±151.7	6.71~481.1	46.78±35.31	17.35~108.2	12.8~1540	50~500	118~310	29~310	76.88~186.1
Hf	2.53±0.99	0.71~4.11	1.14±1.11	0.28~2.98	0.31~15.9	0.8~5	1.2~2.9	1.84~3.4	0.08~1.79
Sr	44.88±34.18	11.3~131.3	90.75±90..17	2.99~223.3	27.4~894	40~600	140~340	33~320	44.38~125.0
Nd	43.4±19.58	15.03~72.54	25.4±19.6	5.39~55.27	3.8~84.8	7~10	6.0~13.0	8.2~14.1	–
Zr	141.9±98.31	29.25~301.3	59.33±50.77	10.88~131.5	–	–	72~170	95~193	–
Cs	3.41±2.89	0.61~9.45	1.67±1.29	0.19~3.09	0.77~33	0.2~3	0.9~3.5	0.29~1.63	0.12~0.33
Tb	0.61±0.32	0.13~1.3	0.62±0.32	0.13~0.94	0.07~2.1	0.08~0.7	0.15~0.31	0.24~0.47	0.01~0.24
Sc	7.66±2.83	3.0~11.51	6.68±3.36	3.11~11.78	0.12~18.3	1~10	3.7~5.5	2.1~11.4	1.17~16.2
Rb	72.42±43.33	15.4~146.9	11.19±11.0	1.91~25.91	1.4~93.8	2~40	5.8~26	2.6~14.2	–
Fe	8983±4012	1158~16720	16720±9495	7866~32120	2000~45000	3000~40000	4900~11400	960~4900	400~52700
Zn	8.47±10.43	2.89~40.7	19.16±14.88	2.34~41.14	0.56~192	5~5000	16.8~270	12.5~79	–
Ta	0.58±0.28	0.25~1.17	0.06±0.06	0.01~0.16	0.07~4.5	0.1~2	0.12~0.33	0.19~0.82	0.08~1.04
Co	13.75±5.12	5.87~23.27	7.17±9.33	1.13~23.48	0.83~25.4	1~40	2.5~6.1	3.7~13.6	0.26~31.86
Eu	1.11±0.52	0.25~1.98	0.95±0.68	0.25~2.04	0.02~2	0.1~0.8	0.27~0.56	0.27~0.99	–
Sb	0.55±0.32	0.09~1.15	0.27±0.39	0.05~0.98	0.05~28.6	0.1~10	0.22~0.78	0.26~1.03	0.08~1.12

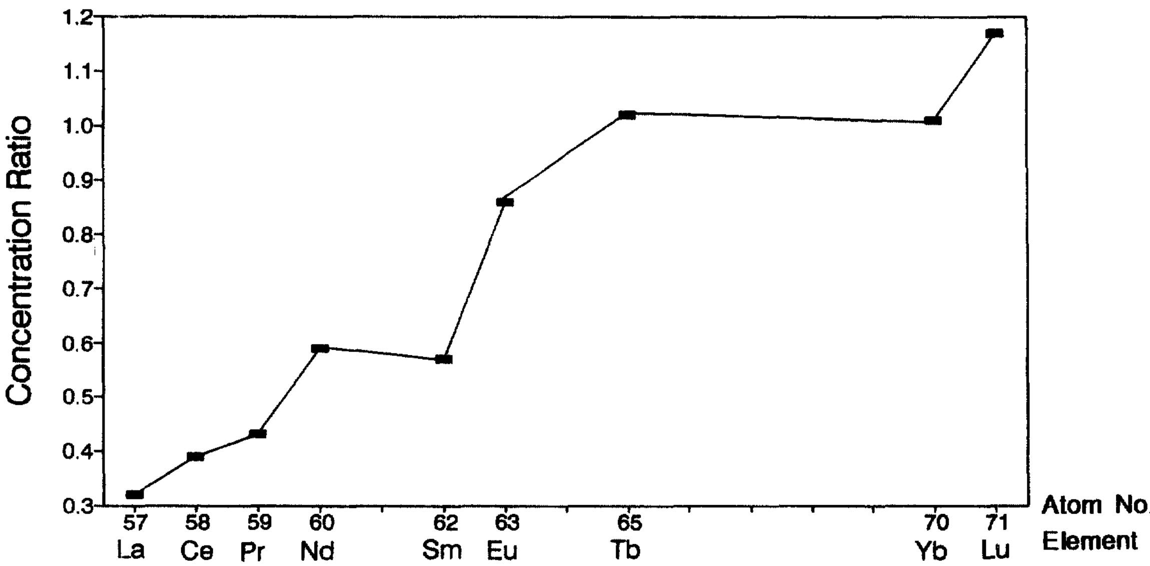

Fig. 1. Distribution of rare-earth elements between two kinds of anthracites (Samcheok / Chungnam).

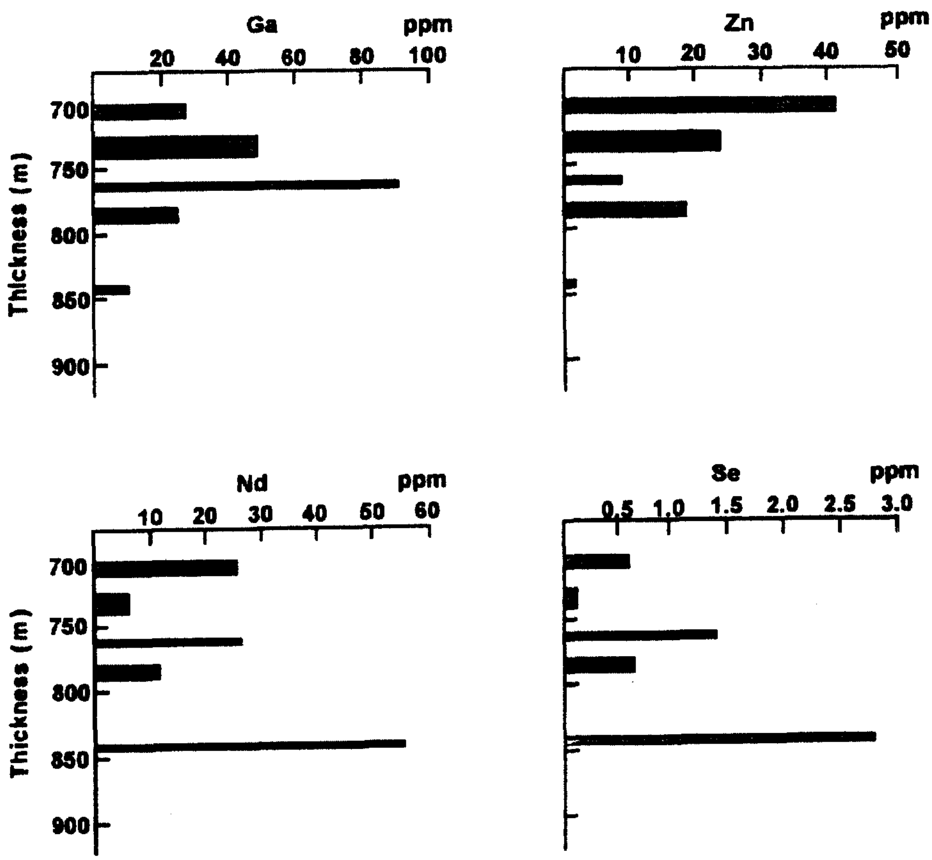

Fig. 2. Examples of vertical distribution of trace elements in Samcheok anthracite seams.

geological meaning of this trend is not yet revealed.

Samcheok coal-field has five seams. The upper 4 seams evolved at the Permian geological period(a little older period). To verify the difference of these two kinds of seams, the vertical distributions of some trace elements in 5 seams were obtained. A few examples are shown in *Fig.* 2. Many elements, including Ga, K, Th, Hf, Sr, Cs, Rb, Zn, Co and Sb, have wide vertical variation. Several elements, such as W, Ga, Sr, Zr and Zn, are present in greater concentrations in upper 4 seams than the lowest seam.

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