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CLUSTERING OF TURKISH LIGNITES FOLLOWING NEUTRON ACTIVATION ANALYSIS*

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ABSTRACT

Trace elements in eleven kinds of coal were determined by thermal neutron activation analysis using the multi-element comparator technique. Coal samples and N.B.S Coal-standard reference material (1632a-Bituminous) were irradiated for 1 min, 10 min and 7 hr at a flux of 10^{12}n/cm^2-s in the University of London Reactor. The spectra were processed using the SAMPO program. The results of different irradiation times were compared to minimize the irradiation time for a particular group of elements. The results were analysed with the CLUSTER ANALYSIS program adapted to PDP11/04 minicomputer to find out the similarity of elemental concentrations for each kind of coal.

ÖZET

Maden Tetkik ve Arama Enstitüsünden temin edilen 11 çeşit kömürde yavaş nötron aktivasyon analizi ile eser element tayini yapılmıştır. Kömür numuneler ve N.B.S kömür standardı (1632a-Bituminous) Londra Üniversitesi Reaktöründe 10^{12}n/cm^2-sn akıda 1 dak. 10 dak ve 7 saat süreyle ışınlanmıştır. 45 cm^3 Ge(Li) dedektörü ve 4096 kanallı analizör ile alınan spektrumlar magnetik teyplere kaydedilerek SAMPO programı ile analizlenmiştir. 10 dakikalık ışınlama süresinin, hem saat hemde dakika mertebesinde yarı-ömürlü izotoplar için kabul edilebilir sonuçlar verdiği saptanmıştır. Sonuçlara "Kümelendirme" (Cluster) Analizi programı uygulandığında; çeşitli yörelerden alınan linyitlerin iki kümeye ayrılabileceği görülmüştür.

INTRODUCTION

Lignite is a very important type of fuel in Turkey. The composition of coal for heating and energy production purposes represents the most common and wide-spread source of atmospheric pollution.

Intrumental neutron activation analysis by using a multi-element standard allows to determine a large number of elements in coal samples /1/.

In 1973, five different kinds of lignite were analysed /2/. The results of analysis of long-lived isotopes of lignites taken from five different zones were published /3/ after this study started.

The present work was carried out on eleven kinds of coal to find out optimum irradiation time for a particular group of elements and to set up similarity of concentrations of the elements

* *This work has been carried out at the University of Surrey, U.K. Statistical analysis has been completed at Ankara Nuclear Research and Training Center.*

for each kind of lignite with cluster analysis.

EXPERIMENT

Eleven different kinds of Turkish coal were supplied by the Mining Research and Exploration Institute of Turkey, (M.T.A). 500 gr solid sample was powderized by a ball-mill for 2-3 hours. 200 mesh powder sample was dried in vacuum at room temperature for 24 hours then 200 mg was weighted into the polyethylene vials (13 mm diameter, 8 mm depth).

The irradiation were carried out in the University of London Reactor at a thermal flux of 1.7×10^{12} n/cm^2-s for 1 min and 10 min irradiations; 1.3×10^{12} n/cm^2-s for 7 hr irradiations. Cobalt wires were used as flux monitors for 7 hr irradiations.

Before counting, the samples were transferred to the clean vials. Cooling periods were 2 min for 1 min irradiations; 10 min for 10 min irradiations and 17 hr for 7 hr irradiations. The samples were counted with a 45 cm^3 Ge(Li) detector connected to a 4096 channel LABEN 8000 series MCA and PERTEC magnetic tape recording unit. Counting periods were 10 min for 1 min and 10 min irradiations and 15 min for 7 hr irradiations. Cobalt wires were counted for 100 sec after a cooling period of one week. The samples were counted either 10 cm or 30 cm away from the detector; dead time was less than 30% in all cases. All peak areas corrected by its own fp (fp = Clock time/live time). Live time was recorded at channel zero of each spectra.

For multi-element analysis, N.B.S Coal (SRM 1632a-Bituminous) standard reference material was used as the comparator. 1632a-Coal Bituminous standard reference material certificate dose not cover all the elements in the samples. Bowen Kale and Orchard Leaves standard reference materials were irradiated for 1 min and 10 min to cover the other elements in the samples.

RESULT AND CONCLUSION

The spectra were processed with the program SAMPO /4/ by using PEAKFIND, SHAPEIN and FITDO, routines on a CDC 6600 computer. For the FITDO routine 20 channels were given on each side of the peaks. The significance limit was 2 for the search and 4 for the fitting.

Qualitative determination was made by using the tables given in Carder /5/ and Erdtmann /6/. Qualitative results are listed in Table-1. Error calculations of concentrations were carried out as the maximum possible error by concerning area errors of sample and standard from the SAMPO program outputs and standard deviation of the certified values given by the N.B.S.

Table-1 shows that 10 min irradiation is quite suitable to determine either short-lived or a few hours half-lived isotopes in Turkish Lignites, too /7,8/. If it were possible to wait for a few weeks for decay, we belive, the long-lived isotopes, e.g. Cr, Fe, Co, Se could also be determined.

When Table-1 was compared with the U.S.A. coal analysis results; it could be seen that either toxic or other element concentrations in some Turkish coals are slightly higher than that of their maximum value in the U.S.A Coals; Table-2 /9,10/.

The lignite results in Table-1 were analysed with the Cluster Analysis Program /11/. The cluster analysis procedure starts from a matrix of similarities which records the relationship between n

objects (the samples) each characterised by m attributes (e.g. measured elemental concentrations). The mean Euclidean Distance, $d_{a,b}$, was used for computation of a similarity measurement between all possible pairs of samples. The distance, $d_{a,b}$, between any two points, a and b, in m-space is defined as:

$$d_{a,b} = \left[\frac{1}{m} \sum_{i=1}^{m} (a_i - b_i)^2 \right]^{1/2}$$

where a_i and b_i are concentrations of element i in samples a and b, respectively ($1 \leq i \leq m$).
The most common way of displaying the results of clustering is a dendogram or a tree diagram.

As it can be seen from Fig. 1, it is possible to classify Turkish lignites mainly in two groups.

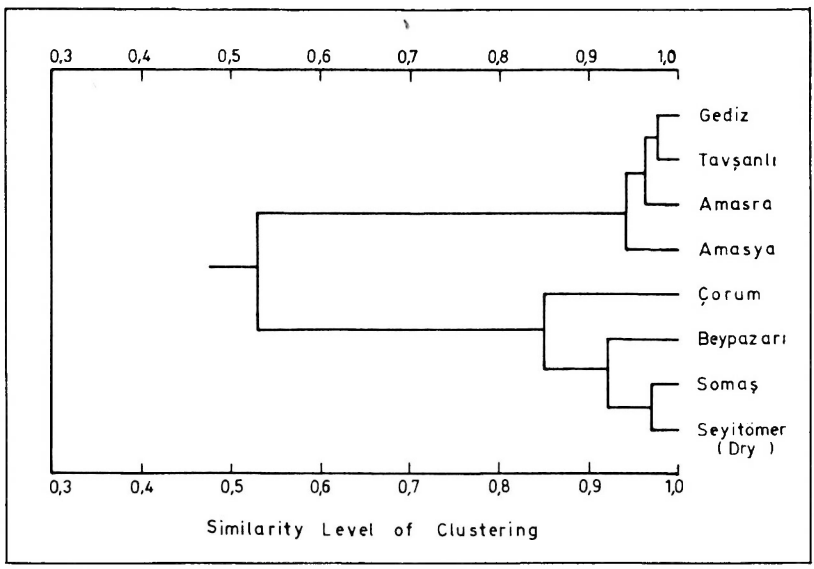


Fig. 1. Dendogram resulting from cluster analysis of Turkish lignites.

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TABLE-1. Elemental concentrations in Turkish coals (ppm)

Element	Isotope	Half Life	Irradiation time	γ-Energy (keV)	+100 Seyit Ömer	Gediz	Tavşanlı	H 8 Çorum ADL
Na	Na^{24}	15h	10m	1368	1539±203	175±29	437±60	2303±299
Mg	Mg^{27}	9.5m	"	1014	4862±376	10367±1101	12212±2203	6101±557
Al	Al^{28}	2.3m	"	1778	2763±401	16754±2514	14444±2150	7036±242
Cl	Cl^{38}	37m	"	2167	42±1	32±5	—	68±6
K	K^{42}	12.5h	"	1524	—	4930±662	3840±561	—
Ca	Ca^{49}	8.8m	"	2061	10570±700	2150±307	4250±442	34880±1530
Ti	Ti^{51}	5.8m	"	320	293±17	1770±72	1360±75	835±29
"	"	"	1m	"	180±79	1480±511	1230±375	574±216
V	V^{52}	3.8m	10m	1434	48±4	71±6	5.6±0.5	40±4
"	"	"	"	"	40±1	48±2	9.5±0.5	31±1
Mn	Mn^{56}	2.6h	7h	846	50±22	40±22	149±73	141±58
"	"	"	10m	1811	36±4	49±5	125±13	76±8
"	"	"	1m	846	34±12	16±5	115±60	109±40
Zn	Zn^{71}	2.4m	10m	389	39±1	30±7	46±9	190±18
As	As^{76}	26.5h	7h	559	16±7	—	90±40	30±13
Eu	Eu^{152m}	9.2h	7h	963	0.16±0.02	0.60±0.05	1±0.06	1.89±0.14
"	"	"	10m	122	0.16±0.03	0.48±0.08	0.65±0.18	1.17±0.30
Ba	Ba^{139}	1.4h	10m	166	123±10	58±16	193±44	86±23

TABLE-1. Elemental concentrations in Turkish coals (ppm) (Cont.)

+ 18 Beypazarı	Somaş	Amasya	Seyit Ömer (Dry)	Coke	Bituminous (Coal Washed) 18-50	Amasra Bituminous
104±14	1153±150	2854±69	1049±136	340±50	759±103	1449±191
8441±816	11047±763	13856±1827	8475±583	—	6159±592	17185±1580
8658±1249	3870±559	21926±3356	2605±373	9885±1447	8674±1262	22677±3350
80±17	57±7	130±16	45±6	277±28	321±31	139±15
—	2030±251	7710±818	—	—	2850±460	—
13290±1115	11640±700	10870±921	11940±608	4050±325	11470±425	5590±402
1720±60	2400±78	2530±78	268±14	1060±165	890±34	1700±60
1780±364	1707±682	2920±643	265±99	1620±399	—	—
121±5	46±4	62±6	44±4	65±6	49±4	57±5
123±6	38±1	88±5	39±1	85±5	—	—
104±50	156±76	420±192	31±14	79±39	414±175	87±49
120±11	66±7	182±19	44±4	86±4	197±20	68±7
106±36	49±14	166±68	31±9	31±9	—	—
—	26±5	50±11	36±5	—	59±10	62±10
254±108	94±42	32±14	12±5	13±5	13±6	4±2
0.35±0.12	1.06±0.60	1.67±0.10	0.12±0.02	0.57±0.03	0.72±0.05	1.27±0.07
0.33±0.09	0.26±0.06	0.95±0.29	0.12±0.03	0.7±0.17	0.57±0.18	1.19±0.3
82±25	41±16	284±65	82±21	283±46	235±45	149±43

m: minute
h: hour
—: data lost

TABLE-2. Comparison of Turkish and U.S.A coals.

Element	TURKISH		U.S.A. /7,9,10/	
	Minimum Value	Maximum Value	Minimum Value	Maximum Value
Al (%)	0.26	2.26	0.31	6.60
Ca (%)	0.21	3.48	0.01	3.80
K (%)	0.20	0.77	0.01	1.40
Mg (%)	0.48	1.71	0.01	0.99
Na (%)	0.01	0.28	0.01	0.60
Ti (%)	0.03	0.29	0.02	0.29
As (ppm)	4	254	0.34	120
V (ppm)	9.5	123	4.8	99

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