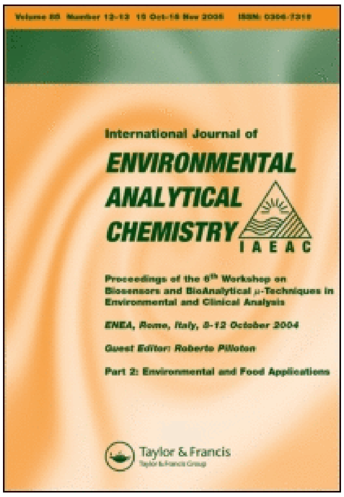

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A Correlation Study of Trace Elements in Lignite and Fly Ash Generated in a Power Station

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A CORRELATION STUDY OF TRACE ELEMENTS IN LIGNITE AND FLY ASH GENERATED IN A POWER STATION

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In the present study, lignite samples of Amynteon lignite field, as well as fly ash and bottom ash samples of Amynteon power station were analyzed for their trace elements content. Chemical analyses were performed by ICP-AES for the elements Sb, Ba, B, Cd, Cr, Co, Cu, Pb, Mo, Ni and Zn and by XRF for Mn, P and F. Trace elements content of lignite samples were correlated with relative ash content in order to determine the geochemical affinity of the elements. An inorganic affinity was found for the elements Ni and Cu, while an organic affinity was indicated for F and an intermediate affinity for the elements Ba, B, Cd, Co, Cr, Mn, Mo, Pb, P, Sb and Zn. Relative enrichment factors were also estimated so as to classify elements according to their partitioning during coal combustion. It is concluded that the elements Sb, B, Ba, Ni, Zn and Cd may be partially volatilized and thus not enriched in the solid residues, while Cr, Co, Cu, Pb and Mo rather condense within the installation and Mn is not depleted nor enriched.

Keywords: Trace elements; lignite; Greece; geochemical affinity; relative enrichment; XRF; ICP-AES

INTRODUCTION

Great amounts of potential hazardous trace elements are released into the environment because of the large quantities of coal consumed, especially for electricity generation. Various pollution control procedures and devices are used by the coal industry to minimize the release of these elements. Analytical chemistry has a very important role in obtaining meaningful data for trace elements in coal and involves at the stages of sampling, analysis and assessment of results. XRF and

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ICP-AES are considered as fast and accurate multielement analytical methods. Attention should be given to possible sources of errors during sample preparation, namely, contamination from reagents or material of the vessel and losses by volatilization. Analytical problems related to ICP-AES will be permanent until we understand the key processes controlling vaporization, ionization and excitation of analyte in plasmas.

Spears and Zheng [1] noted that environmental important trace elements include As, Cd, Pb, Mo, Se and, to a lesser extent, Cu, Ni, Zn, V, U, Cr and F. The US Clean Air Act Amendments [2] identified potential hazardous air pollutants (HAPs) that may be released during the combustion of a coal. HAPs elements include As, Be, Cd, Cr, Co, Hg, Mn, Ni, Pb, Sb, Se and radionuclides (e.g. ^{238}U).

The mode of occurrence refers to how the element is chemically bound and physically distributed throughout the coal. There are important factors in anticipating the behavior of the element during coal cleaning and combustion, as well as during weathering and leaching of the coal and coal waste products. The modes of occurrence can be inferred from indirect evidence, such as statistical correlation with other elements or with other coal characteristics, such as ash yield [3,4].

During coal combustion, some elements are concentrated in the coarse residues (bottom ash) and others volatilize most readily and are concentrated in the vapor or gas phase [5,6]. Thus, relative enrichment factors are used to classify elements according to their partitioning during combustion.

In the present study, trace element concentrations of Amynteon lignite samples, as well as fly ash and bottom ash samples of Amynteon power station, were determined by ICP-AES and XRF analytical methods. Results were used to investigate the geochemical affinity of the elements and the relative enrichment factors, according to the previous mentioned concept.

EXPERIMENTAL

Sampling

Seven lignite samples, named as A5, A7, A9, A11, A12, A14 and A15 were carefully collected from the roof to the floor of active Amynteon lignite mine. Samples were chosen so as to represent the vertical distribution of the lignite seams in Amynteon field. Two samples were also taken from the stockpile (bunker) of Amynteon mine, named as AB1 and AB2. Mined lignite is collected at the bunker, before proceeding to the nearby lignite-fired power station. Two samples, one of fly ash and another of bottom ash were collected from Amynteon power plant. Bottom ash corresponds to the coarse particles (>100 μm), which immediately fall to the bottom of the boiler into a waterfilled vessel under the boiler, whereas fly ash corresponds to fine ash particles (<100 μm), carried along with the flue gases and collected by electrostatic precipitators (ESP). All samples were air-dried at ambient temperature for approximately ten days and then ground to grain size <1 mm.

Analytical methods

Lignite samples were ashed according to DIN standards [7]. The ash content determinations were used for the evaluation of geochemical affinity and relative enrichment factors, as will be described below.

Although sensitive and accurate methods exist for almost all elements in geological samples, for economic reasons the trade-off between quantity, quality and price makes it impossible to use many of the methods on a routine basis. Thus, XRF and ICP-AES are considered as fast, cheap and yet accurate multielement analyses methods in geological prospecting [8,9].

An X-Ray Fluorescence method was applied for the determination of the elements Mn, P and F. Samples were ground down to 40 μm. The apparatus used was a PW 1404 Philips device. Pressed powder disks, with a thickness of 2 mm, were made using 3 g of each sample. Concentrations of the elements were determined by reference to calibration standards, with appropriate corrections being made for instrumental errors and the effects of the composition of the sample on X-Ray emission intensities. The detection limit was 50 $\mu g\ g^{-1}$. The effect of grain size in XRF measurements was tested: two disks, one containing a lignite sample with grain size <0.5 mm and another containing the same lignite sample with grain size <40 μm were analyzed. The results showed that there is no significant effect of grain size. A specialized software program was used for normalizing the values and to correct the possible errors. The organic content of sample (sum of C+H+N) was also considered in the calculations of the program.

ICP-AES was applied for the determination of the elements Sb, Ba, B, Cd, Cr, Co, Cu, Pb, Mo, Ni and Zn. ICP PW 7450 by Philips was the analyzing apparatus. The sample dissolution procedure is critical in at least two respects: first, samples should be completely dissolved to get reproducible and accurate results, and second, nebulizer problems should be avoided. Test solutions containing appropriate concentrations of each element were prepared from a 1000 $\mu g\ ml^{-1}$ reference solutions (MERCK standards). Reliability of the method was verified by the linearity of the calibration curve measuring the standard solutions.

The digestion method followed for the samples of this study included dissolution of the samples by aqua regia, according to DIN standards [10]. 0.5 g of each sample (including 6 duplicates) were diluted to a final volume of 50 ml and warmed for 2 hours until a transparent solution resulted. After filtration, the final solution was ready for ICP analysis. The filters were water-washed, then dissolved by sodium peroxide (Na_2O_2). HF was added in order to achieve complete dissolution. The latest solution was also analyzed for the trace elements under concern. Unless trace elements are found by ICP, the aqua regia digestion method is accepted.

RESULTS AND DISCUSSION

Results of trace element contents of lignite samples, as analyzed by ICP-AES and XRF, are shown in Table I. The ash content of lignite samples is also given.

TABLE I Trace element and ash contents of Amynteon lignite samples

Sample	*A5*	*A7*	*A9*	*A11*	*A12*	*A14*	*A15*	*AB1*	*AB2*
Ash %	14,8	16,1	11,1	10,8	21,2	16,2	26,1	26,5	20
Analyzed by XRF (in $\mu g\ g^{-1}$). Detection limit 50 $\mu g\ g^{-1}$.									
F	1200±72	1100±99	1200±72	1100±99	780±93	1300±104	990±39	1005±40	736±88
Mn	210±19	230±19	<50	<50	110±10	90±10	73±5	77±7	62±5
P	130±9	210±19	170±9	90±9	250±20	700±72	80±9	340±30	500±40
Analyzed by ICP-AFS (in $\mu g\ g^{-1}$). Detection limit 1 $\mu g\ g^{-1}$.									
B	25±1	21±1	14±1	30±1	20±1	80±1	60±1	34±1	18±1
Ba	260±1	423±2	235±1	360±2	353±1	608±2	431±1	375±3	176±1
Cd	5±1	1±1	1±1	1±1	1±1	1±1	1±1	1±1	1±1
Co	5±1	3±1	2±1	1±1	2±1	2±1	1±1	3±1	4±1
Cr	77±1	65±1	24±1	15±1	107±1	42±1	28±1	45±1	35±1
Cu	20±1	19±2	10±1	7±1	25±1	21±1	36±1	22±1	13±1
Mo	76±1	6±1	5±1	1±1	8±1	19±1	13±1	5±1	5±1
Ni	17±1	19±1	11±1	11±1	90±2	25±1	37±1	71±1	45±1
Pb	47±1	9±1	9±1	5±1	7±1	3±1	9±1	4±1	2±1
Sb	204±2	109±13	54±6	68±6	23±2	32±1	51±3	44±1	41±3
Zn	193±1	265±1	164±1	234±1	171±1	407±1	202±2	253±1	129±1

In order to determine the organic/inorganic affinity of the elements, regression diagrams were constructed in which the element concentrations were correlated with the relative ash content of lignite samples. Positive slopes revealed an inorganic affinity, while negative slopes showed organic association. The elemental composition of a coal deposit is influenced by various factors such as the nature of the plant communities, enrichment during plant decay, sedimentation and diagenesis, burial and coalification, and late mineralization [11–14]. On the other hand, the vertical and lateral variation of elements in a coal seam are controlled by the nature of source rocks in the vicinity of the coal basin, the rate of subsidence of the basin and uplift of drainage area and the relation between the drainage area and the coal-forming area [15]. Source material (nature of source rocks), depositional environment, climatic and hydrologic conditions are the controlling factors during the early stages of coal formation, while, rank, tectonic setting and geochemical nature of groundwater and country rocks have greater influence during the coalification stages [16].

The points corresponding to the ash content are plotted versus the contents of every trace element in the nine samples and a simple linear regression analysis has been applied (Figure 1). An inorganic affinity was found for the elements Ni and Cu, while volatile F shows a negative correlation with ash, which may be attributed to organic affinity. An intermediate affinity was deduced for the elements Ba, B, Cd, Co, Cr, Mn, Mo, Pb, P, Sb, and Zn.

During coal combustion in coal-fired power stations, trace elements are enriched or depleted in fly ash and bottom ash. Relative enrichment factors (RE) were introduced by Meij et al. [5] to describe the partitioning of the elements between solid residues and the flue gas. The RE is defined as:

$$\mathrm{RE} = \frac{\text{(Element concentration in ash)}}{\text{(Element concentration in coal)}} \cdot \frac{\text{(\% ash content in coal)}}{100}$$

Calculated RE factors have been used to classify the elements in groups. According to Meij et al., values of RE in fly ash between 0.7 and 1.3 show neither enrichment nor depletion. Values of $\mathrm{RE}<0.7$ in bottom ash and about 1 in fly ash show that the element is condensed within the installation. If $\mathrm{RE} \ll 1$ in bottom ash and fly ash, then the element is very volatile and concentrates to flue gases.

In the present work RE factors were estimated using the average concentration of each element in bunker lignite samples [(AB1+AB2)/2] and the element's concentration in fly ash and bottom ash. Calculations of RE factors are shown in Table II, along with trace elements content of fly ash, bottom ash and bunker samples. Results showed that elements Sb, B, Ba, Ni, Zn and Cd may be partially volatilized and thus not enriched in the solid residues, while Cr, Co, Cu, Pb and Mo rather condense within the installation and Mn is not depleted nor enriched.

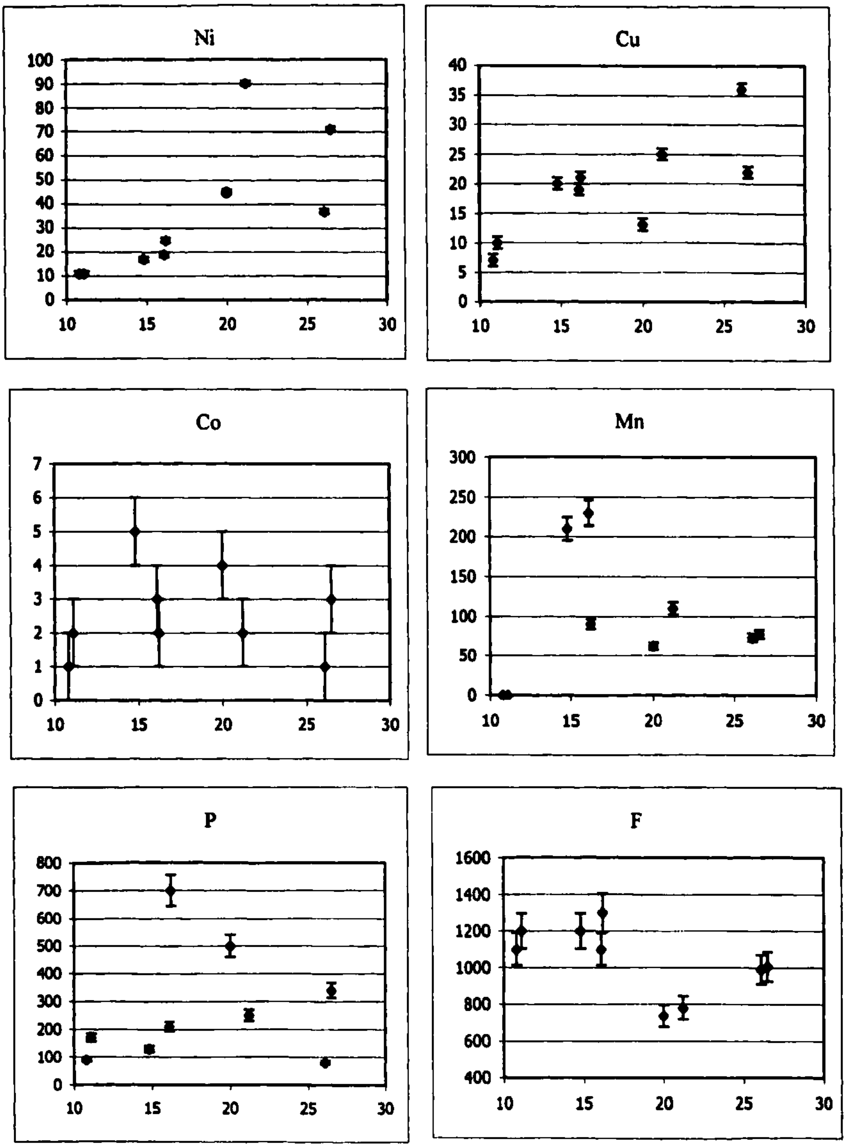

FIGURE 1 Trace element concentrations (in $\mu g\ g^{-1}$) versus ash content (in %weight) of lignite samples. Organic affinity: F. Inorganic affinity: Cu, Ni. Intermediate affinity: Co, Mn, P

TABLE II Trace elements content of the fly ash, bottom ash and bunker lignite samples, and relative enrichment factors (RE) of bottom ash (ba) and fly ash (fa)

	(AB1+AB2)/2	*Bottom ash*	*Fly ash*	*REba*	*REfa*
	Analyzed by XRF (in $\mu g\ g^{-1}$), detection limit 50 $\mu g\ g^{-1}$				
F					
Mn	70	460±36	670±53	1.5	2.2
P	420	700±56	1200±96	0.4	0.7
	Analyzed by ICP-AES (in $\mu g\ g^{-1}$), detection limit 1 $\mu g\ g^{-1}$				
B	26	52±1	52±1	0.2	0.2
Ba	276	375±2	603±3	0.3	0.5
Cd	1	1±1	1±1	0.2	0.2
Co	4	18±1	30±1	0.2	1.7
Cr	40	97±1	147±1	0.6	0.9
Cu	18	35±2	70±1	0.1	0.9
Mo	5	11±1	27±1	0.5	1.3
Ni	58	44±1	60±1	0.2	0.2
Pb	3	5±1	12±1	0.4	0.9
Sb	43	33±4	41±4	0.2	0.2
Zn	191	162±1	198±1	0.2	0.2

More lignite samples of the same region should be analyzed and the results should be compared with the suggested ranges of values for most coals and other published results. Very high contents of environmentally sensitive elements indicate that further investigation is needed to ascertain whether the sample is representative of a large amount of coal or only of a localized area [17]. Amynteon lignites show high concentrations for the elements Sb, B, Mo, Zn and Cd in comparison with worldwide values. Thus, only Sb, B and Cd may be detrimental due to their tendency to volatilize, whereas Mo and Zn condense within the burning chambers. Moreover, the current tendency for coals to be cleaned, prior to combustion, and the use of more efficient particle-attenuation procedures, cause a reduction in the amounts of trace elements in stack emissions relative to those in the bottom ash and fly ash. Hence, more attention should be given to the fate of trace elements in coal wastes, and more particular to losses by leaching to nearby waters [12].

CONCLUSIONS

Chemical analyses of trace element contents in Amynteon lignites were performed by XRF and ICP-AES. The results were used in the determination of the geochemical affinity of the elements and the relative enrichment in fly ash and bottom ash. The elements Cu and Ni have an inorganic affinity, F shows an organic association and Ba, B, Cd, Co, Cr, Mn, Mo, Pb, P, Sb and Zn show an intermediate affinity. Relative enrichment in flue gases with a detrimental potential show the elements Sb, Cd and B, while Mo and Zn rather condense within the installation of power plants.

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