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DETERMINATION OF COBALT, CHROMIUM, MANGANESE AND NICKEL IN PAKISTANI COALS BY ATOMIC ABSORPTION SPECTROMETRY

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Some trace elements (cobalt, chromium, manganese and nickel) have been determined in the coal samples from Pakistani mines. Pakistani coals are mainly sub-bituminous with high contents of sulphur. The above elements do not appear to occur in high concentrations in Pakistani coals. Range of manganese concentration (9.7-42.0 ppm) was much lower than U.S. and world averages. Large scale combustion of Pakistani coals would thus not appear to lead to the unusual environmental pollution due to these trace elements.

Key words: Coal, Trace elements, Atomic absorption spectrometry.

Introduction

Combustion of coal leads to the mobilization of many elements occurring in traces in coal. Consumption of coal would increase to 7 million tons by 1993 although bulk of it will be used by brick kiln industry but the remaining quantity will be utilized for power generation and other uses. Indigenous coal now plays an insignificant role in power generation in the country but the coal based power generation capacity may increase to 280 MW by 1993 leading to more coal consumption at the power plants [1].

Increased coal consumption, in general and specially at the power plant sites may lead to the environmental pollution. A study has, therefore, been initiated to determine trace elements in the coal samples from various Pakistani mines to observe the possible effects of the mobilization of these trace elements on the environmental pollution. Results of the determinations of cobalt, chromium, manganese and nickel in Pakistani coals are reported here.

Experimental

Representative coal samples were collected from mines in the provinces of Sindh (Jhampir, Lakhra and Sonda), Punjab (Khoshab, Makerwal, Sor Range), Baluchistan (Sharigh) and Azad Kashmir (Kotli) . The samples were ground to 60 mesh and ashed at 650° in a muffle furnace. Proximate and sulphur analyses were done on LECO proximate analyser (MAC-400) and sulphur determinator (SC- 132). The results of proximate and sulphur analyses and calorific values are given in Table 1. Calorific values were determined on Parr oxygen adiabatic bomb calorimeter. Perkin Elmer Model 3030B was used for trace element determinations.

All used chemicals and reagents were of analytical grade while standards for elements for atomic absorption analysis were of AA grade. Distilled deionized water was used for the preparation of aqueous solutions.

Boric acid solution was obtained by dissolving 60 g of boric acid in 1 L of water. Aqua regia was prepared by mixing 1 part nitric acid (sp. gr. 1.42) with 3 parts hydrochloric acid (sp. gr. 1.19).

Following general procedure was used for preparation of solutions for atomic absorption analyses by ASTM method [2]. Coal (60 mesh) was ashed and coal ash (0.2 g) was mixed with aqua regia (3 ml) and hydroflouric acid (48% , 5 ml) in a screw capped plastic bottle and placed on a hot water bath for 2 hrs.

Boric acid solution (50 ml) was then added mixture was diluted with water (100 ml) and the solutions were stored in polyethylene bottles.

Standard solutions (1-5 ppm) for atomic absorption analyses were prepared by dilution of stock solutions (1000 ppm) of each element by 10% hydrochloric acid solution.

The samples were analysed by recommended procedures under the standard conditions [3] for Cr, Co, Mn and Ni. A blank was run at the time of the determination of each element by aspirating an aqueous solution containing aqua regia and boric acid in the same concentrations as those of coal samples

TABLE 1. PROXIMATE AND SULPHUR ANALYSES AND CALORIFIC VALUES OF PAKISTANI COALS.

S. No.	Name of the source of the sample	Moisture content (%)	Ash content (%)	Volatile matter content (%)	Fixed carbon content (%)	Sulphur content (%)	Calorific value (Btu/lb)
1.	Jhampir	20.7	6.43	43.64	29.23	2.34	9,525
2.	Khoshab	6.2	16.8	39.66	37.34	3.21	9,190
3.	Kotli	8.6	5.91	46.62	38.87	3.34	11,600
4.	Lakhra	9.56	9.08	42.48	38.88	4.48	10,205
5.	Makerwal	3.37	22.32	38.31	35.64	7.04	9,250
6.	Sharigh	7.66	5.65	42.41	44.28	1.65	10,445
7.	Sonda	8.93	6.81	45.65	38.62	3.1	10,270
8.	Sor Range	9.03	6.74	39.77	44.64	2.37	10,950

and standard solutions. The burner type and orientation, fuel selection and recorder expansion were selected in such a manner as to allow determination of the elements directly from 100 ml coal ash solution without any further dilution.

Results of the concentrations of the determined trace elements are given in Table 2.

TABLE 2. DETERMINATION OF TRACE ELEMENTS IN PAKISTANI COALS AND COMPARISON WITH ELEMENT CONTENTS IN SOME OTHER COALS (VALUES IN PPM).

S. No.	Name of the source of the sample	Co	Cr	Mn	Ni
1.	Jhampir	49.8	35.7	9.7	9.6
2.	Khoshab	94.9	68.1	42.2	25.2
3.	Kotli	13.9	19.8	20.6	10.9
4.	Lakhra	67.3	24.5	9.9	14.9
5.	Makerwal	155.3	72.5	-	22.3
6.	Sharigh	43.5	28.0	11.3	9.9
7.	Sonda	30.5	30.2	20.3	33.9
8.	Sor Range	5.0	2.3	15.8	15.8
9.	U.S.Average[5b]	7.0	15.0	1200.0	15.0
10.	Worldwide Average[5b]	5.0	10.0	200.0	15.0
11.	U.S.North Great Plains (Lignite)	0.05[5e]	0.25-43[5d]	7.3-66u[5e]	0.52-84[5f]
12.	U.S.North Great Plains (Sub-bituminous)	0.25-20[5e]	0.54-60[5d]	1.4-450[5e]	0.32-6/[5f]
13.	U.S.Appalachian (Bituminous)	0.7-930[5e]	1.5-220[5d]	0.75-1400[5e]	1.1-220[5f]

Not detected (<0.05 ppm)

Results and Discussion

Atomic absorption spectrometry is a useful technique for determination of various elements in coal. It has been used for the determination of Co, Cr, Mn, Ni [4a] and this technique was used also for determination of these elements in Pakistani coals.

Among these trace elements, it has been suggested that Co, Cr and Ni occur in sulphide minerals and in organometallic compounds as chelated species or as adsorbed cations in coal [5a]. Manganese is mainly associated with the inorganic matter in coal [5a,6].

Cobalt and chromium in Pakistani coals were higher than U.S. and world averages [5b] but Co was within the range of U.S. Appalachian bituminous coals [5c] while chromium was within the range of U.S. Rockey mountain and Appalachian coals. [5d].

Managanese concentration (9.7 -42.0 ppm) in Pakistani coals is much less than U.S. (1200 ppm) and world wide (200 ppm) averages. Managenese was not detected in the coal sample from Makerwal mine. Manganese content in Pakistani coals was similar to the range reported for managenese (8.5 - 90 ppm) in the coal samples from Nebraska, U.S. A. [5e].

Nickel in the Pakistani coal samples varied in the range (9.6 - 33.9 ppm) and nickel content in most of these samples was close to the U.S. (15 ppm) and worldwide (15 ppm) averages. Nickel range for world coal is 0.5 - 50 ppm Ni. Nickel concentrations in coal samples from Nebraska (USA) ranged from 5 - 200 ppm [5f].

Conclusion

Chromium and nickel are potentially toxic and are considered to be of moderate environmental concern in coal [4b]. Manganese promotes conversion of sulphur dioxide into sulphuric acid, the most irritating sulphate form [4c] and is considered to be of minor environmental concern alongwith cobalt in coal [4c]. There are other trace elements also possibly of greater environmental concern like arsenic, selenium, lead, copper, zinc, mercury and cadmium and this work could be expanded in future to determine the concentrations of these elements also in Pakistani coals.

The environmental pollution from coal-fired power stations can occur from a number of coal combustion products like gaseous and particulate emissions and from waste ash disposal. It is the chemical form of trace element and its mobility from waste ash dumps that determines the extent of pollution alongwith the atmospheric release of gas and particulates posing further environmental problems.

The studied elements (Co, Cr, Mn, Ni) do not appear to be in high concentrations in Pakistani coals and thus their mobilization of large scale utilization of Pakistani coals should not lead to any unusual pollution of the environment due to the presence of these trace elements in coal. However, 8 samples are not enough and more samples will need to be analysed to give an unequivocal judgement.

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