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DETERMINATION OF FLUORINE IN COAL AND COAL FLY ASH BY PROTON-INDUCED GAMMA-RAY EMISSION ANALYSIS

KEYWORDS: Fluorine, PIGE, coal, fly ash

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ABSTRACT

The fluorine concentration in NIST, SARM, and Argonne Premium coal and coal fly ash standards was determined by external-beam proton-induced gamma-ray emission (PIGE) analysis using both the method of standard additions and the comparative method. The $^{19}F(p,p_1)^{19}F$ E_γ = 110 keV and $^{19}F(p,p_2)^{19}F$ E_γ = 197 keV reactions at 2.5 MeV were utilized. A minimum detection limit of *c.a.* 10 ppm was obtained for both coal and coal fly ash. The relative standard deviation of a single measurement ranged from 2 to 20%. Good agreement was observed between the PIGE results and the fluorine values obtained by the pyrohydrolysis method. The advantages of this technique over conventional methods of fluorine analysis are its speed, sensitivity, non-destructive nature, and simple sample preparation procedure.

INTRODUCTION

Fluorine is an essential trace element which is toxic at high concentration levels. Skeletal fluorosis, which is characterized by increased bone thickness and stiffness of joints, occurs in humans and animals when they ingest excessive quantities of fluoride. The disease is endemic in areas with soils and waters that contain high levels of fluoride and has occurred in non-endemic areas as a result of industrial pollution.[1]

Fluorine occurs in trace amounts in most coals. It is typically associated with minerals of the apatite group, principally fluorapatite and clays, and with fluorite, tourmaline, topaz, amphiboles and micas.[2] The average fluorine content of US coal is, according to the tabulation of Swanson *et al.*[3], 74 μg/g. In the United States, the lowest average fluorine concentration of 30 μg/g is found in coals from Eastern Kentucky and the highest average value of 160 μg/g is found in coals from Wyoming and New Mexico.[4] The concentration range of fluorine in European coals is similar to that found in the US while the average fluorine content of Australian coals ranges from 15 to 500 μg/g.[5]

Fluorine is released into the atmosphere during the combustion of coal. According to a National Academy of Sciences report, coal combustion accounts for a significant fraction (10%) of the total atmospheric emissions of fluorine in the United States.[6] Because of its effect upon environmental quality and health, fluorine has been classified as an element of moderate concern in the development of the coal resource.[7] With the increased utilization of this energy resource, it is

important to be able to reliably determine the fluorine content of coals and coal by-products.

The amount of fluorine in coals and geological materials is generally determined using an ion selective electrode or, more recently, ion chromatography to measure the concentration of fluoride ions in a solution prepared from the sample. The most common chemical pretreatment techniques include alkali fusion,[8,9] oxygen bomb digestion,[2,8] and pyrohydrolysis.[2,8,10,11,12] The ASTM standard method (D3761-79) is based on the oxygen bomb procedure; a simple and convenient sample preparation technique. The validity of the oxygen bomb and alkali fusion methods has, however, been called into question as these two procedures consistently yield lower results than those obtained by pyrohydrolysis.[8,10,13] This is most likely due to the incomplete dissolution of fluorine from the sample by these two procedures. The end result of this discrepancy is a wide range of fluorine values in the literature and the lack of certified fluorine values for coal and fly ash standards.

In order to aid the certification process, we have determined the fluorine content of several coal and fly ash standards by an alternate method; proton-induced gamma-ray emission (PIGE) analysis. PIGE is a rapid, non-destructive analysis technique that can be *instrumentally* applied to the determination of low-Z elements in complex matrices.[13,14] It has been used to determine the fluorine content of various geological materials[15,16] and of the NIST 1632a and 1633a coal and fly ash standards.[11,17] We have, using both the method of standard

additions and the comparative method, determined the fluorine content of several NIST, SARM, and Argonne Premium coal and fly ash standards by PIGE.

EXPERIMENTAL PROCEDURE

Sample Preparation. For the standard addition measurements, one blank and four spiked samples were prepared from each standard. The spiked samples were prepared by adding appropriate amounts of the NIST fluorine spectrometric solution (SRM 3183) to approximately 200 mg of each standard and mixing in a s.s. mortar mixer mill for 15 minutes. The blank and spiked samples were then pelletized in a 13-mm s.s. die at 90 Mpa. It was found that the volume of added spike must be kept below 50 μL in order to ensure no fluorine loss during pelletization. Cellulose powder (Whatmann CC31) was mixed with the NIST 1633a fly ash standard in order to obtain a stable pellet. The blank and spiked samples of NIST 1633a were prepared from this mixture. No fluorine was detected in a blank pellet of the cellulose powder. Two sets of standard addition samples of each coal and fly ash standard were prepared and analyzed.

For the comparative measurements, two samples of each standard were prepared. In these measurements, a fly-ash/graphite mixture (30 wt. % ash) was used for the NIST 1633a sample. Again, no fluorine was detected in a blank graphite pellet (Johnson Mathey, Ultra 'F' Carbon Powder).

PIGE Analyses. The measurements were performed at the University of Kentucky 7.5 MV Van de Graaff accelerator.[18] A HpGe detector with a full-width at half-maximum (FWHM) resolution of 2.4 keV at 1274 keV was placed 3.0 cm

from the target at an angle of 90° relative to the beam direction. Both the 110- and 197-keV γ-rays from the proton inelastic scattering reaction were used. All irradiations were performed at 2.5 MeV (on target) with an external proton beam in air. The beam, normal to the target surface, was rastered over the sample at 1 Hz irradiating a spot of 5 mm by 7 mm. The proton beam current, on the extraction foil, ranged from 50 to 100 nA and the irradiation times were adjusted to obtain a statistical uncertainty of less than 10% for the area of the 110- and 197-keV γ-ray peaks. The irradiation times ranged from 3 to 15 minutes. Rather than adjust the beam current to maintain a constant count rate, a pulser was used to correct for the dead time in the PIGE spectra. As an example, the PIGE spectrum of the NIST 1632a standard is shown in Figure 1.

In order to determine if the concentration of the fluorine changed during the proton irradiation, the NIST 1632a sample pellet with a 342 ppm fluorine spike was subjected to seven consecutive three minute irradiations at 70 nA. As can be seen in Figure 2, no significant variation was observed in the normalized 110- and 197-keV γ-ray yields in the multiple bombardments. The normalized γ-ray yield is simply the dead-time corrected peak area divided by the charge accumulated on the beam extraction foil.

RESULTS AND DISCUSSION

A typical example of the standard addition curves obtained in the analyses is given in Figure 3. The fluorine results for the NIST, SARM and Argonne Premium coal standards obtained by the PIGE standard addition and comparative

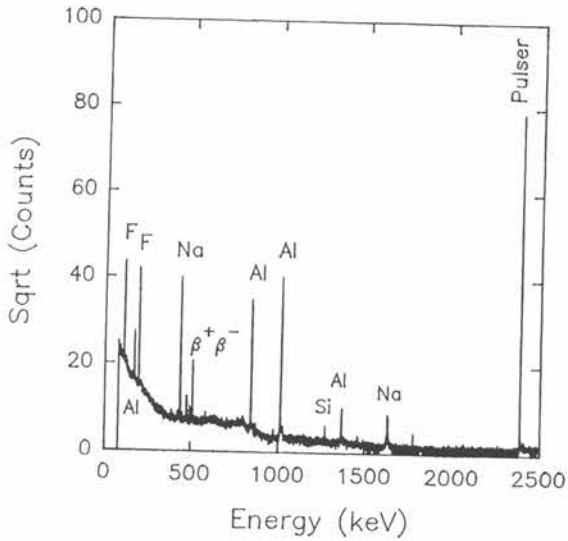

FIG 1. The thick-target PIGE spectrum of NIST 1632a (bituminous coal). The spectrum was accumulated with a 2.5 MeV proton beam at an average current of 50 nA.

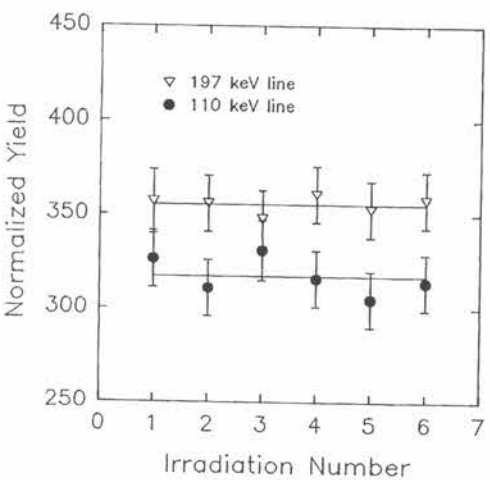

FIG 2. The normalized 110- and 197-keV γ-ray yields from a spiked NIST 1632a (342 ppm) sample from six consecutive irradiations at an average beam current of 70 nA.

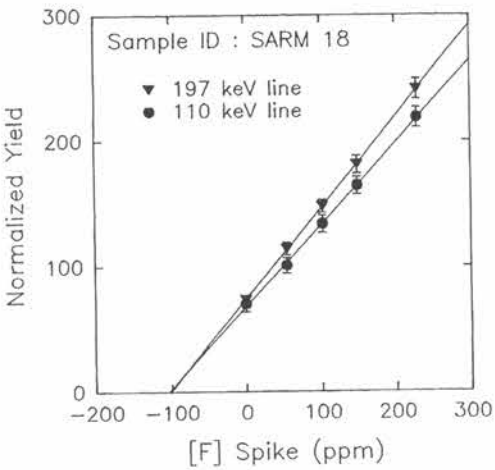

FIG 3. The fluorine standard addition curve for SARM 18. The fluorine concentrations from the 110- and 197-keV lines are 104 ± 3 ppm and 101 ± 1 ppm, respectively.

measurements are given in Table 1. The standard addition PIGE results are the weighted average of the concentration values obtained from the 110- and 197-keV standard addition curves on two series of standard addition samples. The relative standard deviation for a single measurement from either the 110- or 197-keV standard addition curve ranged from 2% to 20% while the norms of the standard addition curves ranged from 0.25 to 2.5. The limits of detection (*LOD*) were calculated by:

$$LOD = 3 * \sqrt{BKG} * F_o / N_o$$

where N_o is the area under the γ-ray peak, *BKG* is the background over 1 FWHM about the peak's centroid, and F_o is the concentration of fluorine in the blank sample.

TABLE 1
Fluorine Concentrations* (μg/g) of NIST, SARM and Argonne Premium Coal and Fly Ash Standards Determined by Standard Addition and Comparative PIGE Measurements.

Sample	Ash (wt. %)	Standard Addition	Comparative^	LOD (μg/g)
NIST 1632a	21.8	164 ± 9		5
NIST 1632b	6.8	50 ± 2	42 ± 5	5
NIST 1635	4.7	28 ± 2		5
NIST 1633a	100	83 ± 1	83 ± 4	13
SARM 18	10	103 ± 1	102 ± 5	5
SARM 19	28.7	75 ± 6	85 ± 5	6
SARM 20	35.3	125 ± 3	138 ± 6	8
Penn Upper Freeport (UF)	13.5	95 ± 4	86 ± 12	5
North Dakota Lignite (ND)	9.5	34 ± 7	35 ± 6	6
Stockton Seam Bituminous (WV)	19.4	142 ± 12	131 ± 29	7
Blind Canyon Seam (UT)	4.6	60 ± 7	56 ± 7	8
Pocahontas #3 Bituminous (POC)	5.3	19 ± 3	20 ± 4	5
Wyodak Subbituminous (WY)	8.5	59 ± 3	56 ± 9	5
Illinois #6 Bituminous (IL)	16.2	86 ± 6	86 ± 7	5
Pittsburgh #8 Bituminous (PITT)	9.2	122 ± 10	92 ± 38	7

*Dry weight.
^The average value from five irradiations.

As can be seen from the comparison presented in Table 2, the fluorine concentration values obtained in this work for the NIST and SARM standards agree well with the values obtained by pyrohydrolysis and previous PIGE measurements. The fluorine values obtained by oxygen bomb digestion are, on the other hand, consistently lower than the PIGE and pyrohydrolysis values. As noted above, this is most likely due to the incomplete dissolution of fluorine from the sample by this sample preparation procedure.

TABLE 2
Fluorine Concentrations for NIST and SARM Standards Obtained by PIGE, Pyrohydrolysis, and Oxygen Bomb Digestion.

Sample	This Work	Other PIGE	Pyrohydrolysis	Oxygen Bomb
NIST 1632a	164 ± 9	162[16],178[17]	176[2],177[10],175,168[12]	131,128[2],167,158[12]
NIST 1632b	50 ± 2	40[8]	46[8],58,80[11]	
NIST 1635	28 ± 2		39[8],42,85[11],34,35[12]	18,12[12]
NIST 1633a	83 ± 1	87[16],110[17]	82[8],73[10],55,81[11], 89,84[12]	25,22[12]
SARM 18	103 ± 1	114[10]	115[8],107[10],112,117[12]	90,92[12]
SARM 19	75 ± 6	93[10]	96[2],105,103[8],95[10], 102,100[12]	63[2],80,71[12]
SARM 20	125 ± 3	153[10]	148[2],152[8],142,140[11], 129,132[12]	86[2],107,110[12]

Although the Argonne Premium whole coal samples are now widely used by the coal research community,[19] relatively little work has been done on determining the trace element composition of these materials. Of the more than 340 references listed in the Users Handbook for these reference materials,[20] only three papers report trace-element concentration data.[9,21,22] Of these three papers, only one presents data for fluorine. Doughten and Gillison have used alkali fusion and an ion-selective electrode to determine the fluorine content of the Argonne Premium coal samples.[9] The PIGE results reported in this work are, for every sample except the North Dakota Lignite, consistently lower than the values reported by Doughten and Gillison. In the instrumental PIGE analyses, any spectral interference with the 110- or 197-keV γ-rays from the $^{18}O(p,\gamma)^{19}F$ reaction would have been observed with the NIST and SARM samples as the interference

would yield fluorine results that were systematically high. Likewise, it is unlikely that the differences are a result of proton range effects as all of the samples (NIST, SARM, and Argonne Premium) were ground to - 100 mesh. We therefore suggest that the discrepancy could have been caused by contamination in the alkali fusion sample preparation procedure. Further measurements, ideally by an alternate technique such as pyrohydrolysis, are needed to resolve the observed differences.

In addition to the standard addition measurements, the fluorine concentration of the SARM and Argonne Premium coals was determined by comparison of the normalized γ-ray yields from these samples with the normalized yields from either the NIST 1632a or NIST 1635 coal SRM. In the comparative method, the concentration of an element (C) is determined by:

$$C = C_{std} \times \frac{Y \times S}{(Y \times S)_{std}}$$

where Y is the normalized γ-ray yield and S is the stopping power at 2.5 MeV. NIST 1635 was used as the comparative standard for those samples with a fluorine concentration of less than 100 ppm; the remaining samples were compared to NIST 1632a. In each case, the fluorine value obtained by the PIGE standard addition measurement (Table 1) was used as the concentration for the comparative standard. The values obtained from the comparative method are given along with the standard addition results in Table 1. The good agreement between the values in Table 1 indicates that fluorine can be reliably determined in coal and fly ash by the comparative method. This is important for any study

of a large number of samples as the comparative procedure allows the analyst to take full advantage of the speed of the instrumental PIGE analysis.

CONCLUSION

PIGE is a rapid, non-destructive analytical technique that can be used to accurately determine the fluorine content of coal and fly ash. The results from the direct instrumental analysis using the method of standard additions provide, with the pyrohydrolysis results, a reasonable basis for assessing the fluorine content of the NIST and SARM standards. Moreover, a comparison of the PIGE results with those obtained by oxygen-bomb combustion and pyrohydrolysis indicates that the standard ASTM method should be replaced. In this case, sample preparation by pyrohydrolysis followed by an ion-selective electrode or ion chromatography is the most obvious choice for a standard method for the determination of fluorine as few analysts have access to an accelerator.

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