

FLUORINE IN COAL AND COAL BY-PRODUCTS

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INTRODUCTION

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 micas¹. The average fluorine content of US coal is, according to the tabulation of Swanson *et al.*², 74 $\mu\text{g/g}$. In the United States, the lowest average fluorine concentration of 30 $\mu\text{g/g}$ is found in coals from Eastern Kentucky and the highest average value of 160 $\mu\text{g/g}$ is found in coals from Wyoming and New Mexico.³ 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 $\mu\text{g/g}$.⁴

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.⁵ 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.⁶ 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,^{7,8} oxygen bomb digestion,^{1,7} and pyrohydrolysis.^{1,7,9,10,11} 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.^{7,9,12} 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 is based upon the detection of the prompt gamma rays that are emitted following a charged-particle-induced nuclear reaction. The energy of the gamma ray is indicative of the isotope present, and the intensity of the gamma ray is a measure of the concentration of the isotope. This ion beam technique is mainly used in the analysis of light elements. It has been used to determine the fluorine content of various geological materials^{13,14} and of the NIST 1632a and 1633a coal and fly ash standards.^{10,15} We have, using the method of standard additions, determined the fluorine content in NIST bituminous coal SRM 1632b, subbituminous coal SRM 1635, coal fly ash SRM 1633a, USGS Lower Bakerstown coal CLB-1, CANMET BCR 40 and SARM 20.

EXPERIMENTAL PROCEDURE

The PIGE measurements were performed at the University of Kentucky 7.5 MV Van de Graaff accelerator.¹⁶ The nuclear reactions utilized in these PIGE measurements are $^{19}\text{F}(p,p_1)^{19}\text{F}$, $E_\gamma = 110$ keV and $^{19}\text{F}(p,p_2)^{19}\text{F}$, $E_\gamma = 197$ keV. The samples were irradiated with an external 2.5 MeV proton beam in 1 atm. of He. The γ rays were detected with an ORTEC HPGe detector, 20% relative efficiency, with a FWHM resolution of 2.40 keV at 1274 keV. 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 100 to 150 nA, and the collected charge ranged from 90 to 140 μC . The irradiation times were adjusted to obtain an uncertainty in the counting statistics of less than 5% (except for SRM 1635, where the uncertainty was less than 10% after 20 minutes of counting time) in the areas of the 110- and 197-keV γ -ray peaks. The irradiation time per sample ranged from 15 to 20 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 γ -ray spectra. Typically, the dead time in the measurements was less than 3%.

For the standard addition measurements, one blank and four spiked samples were prepared for each coal standard. The spiked samples were prepared by adding appropriate amounts (from 5 to 25 μL) of the NIST SRM 3183 fluoride ion chromatographic solution ($[\text{F}^-] = 1000$ $\mu\text{g/g}$) to

approximately 250 mg of coal. The concentration of fluorine spikes ranged from 25 to 90 $\mu\text{g/g}$. After addition of the fluorine solution, the spiked samples were oven dried for 24 hours at 50°C. The dried samples were then mixed in a polystyrene vial with a methacrylate ball for 30 minutes. The blank and spiked samples were then pelletized in a 13-mm stainless steel die at 90 Mpa. High purity graphite powder (Johnson Mathey, Ultra 'F' spectroscopic grade) was mixed with the NIST 1633a fly ash SRM in order to obtain a stable pellet. The blank and spiked samples of NIST 1633a were prepared from this mixture. Two sets of standard addition samples were prepared and analyzed for each standard. Figures I and II show the typical fluorine standard addition curves obtained.

RESULTS AND DISCUSSION:

The results obtained from the standard addition method for each standard are listed in Table I. The fluorine values, which are reported on a dry weight basis, 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 limits of detection (LOD) for the measurements (Table I) are based on a minimum observable peak area of 3**v**bkg where bkg is the background over 1 FWHM about the gamma-ray (197 keV) peak's centroid. The LOD for fluorine in coal ranged from 2 to 8 $\mu\text{g/g}$, depending upon the ash content in the coal. The relative standard deviation for a single measurement, based upon counting statistics, ranged from 0.9 % to 10 %.

In order to determine if the concentration of the fluorine changed during the proton irradiation, a single pellet of NIST SRM 1632a sample was subjected to four consecutive 15-minute irradiations at 150 nA. No significant variations were observed in the normalized 110- and 197-keV gamma-ray yields in the multiple bombardments. The average normalized yield was $133 \pm 2 \text{ } \gamma\text{/s}/\mu\text{C}$ for the 110-keV gamma-ray peak, and $145 \pm 1 \text{ } \gamma\text{/s}/\mu\text{C}$ for the 197-keV gamma-ray peak. The overall average of the normalized yield for SRM 1632a during four days of consecutive measurements (10 irradiations) was $126 \pm 6 \text{ } \gamma\text{/s}/\mu\text{C}$ for the 110-keV gamma-ray peak, and $141 \pm 6 \text{ } \gamma\text{/s}/\mu\text{C}$ for the 197-keV gamma-ray peak.

As can be seen from the comparison presented in Table II, the fluorine concentration values obtained in this work for the NIST, SARM and BCR standards agree well with the values obtained by pyrohydrolysis. 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.

We are currently using PIGE as a rapid, instrumental technique to investigate how fluorine partitions in wet and dry FGD equipped coal combustion systems. Results from this study will be presented.

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TABLE I

Fluorine Concentrations* ($\mu\text{g/g}$) of NIST, SARM, CLB and BCR Coal and Fly Ash Standards Determined by Standard Addition PIGE Measurements.

Sample ID	Fluorine ($\mu\text{g/g}$)	Ash (wt%)	LOD ($\mu\text{g/g}$)
NIST 1635	28 ± 1	4.7	6.2
NIST 1632b	48 ± 2	6.8	3.9
SRM 1633a	93 ± 10	100	15
CLB-1	68 ± 7	-	2.0
BCR 40	114 ± 6	-	5.9
SARM 20	148 ± 13	35.3	4.6

* Dry weight.

TABLE II

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

Sample ID	PIGE	Pyrohydrolysis	Oxygen Bomb
NIST 1635	28 ± 1	$39^7, 42^{10}, 34, 35^{11}$	$18, 12^{11}$
NIST 1632b	48 ± 2	$46^7, 58^{10}$	
NIST 1633a	93 ± 10	$82^7, 73^9, 81^{10}, 89^{11}$	$25, 22^{11}$
BCR 40	114 ± 6	$128^{10}, 122, 119^{11}$	107^{11}
SARM 20	148 ± 13	$148^1, 152^7, 141^{10}, 130^{11}$	$86^1, 107, 110^{11}$

FIGURE I
Fluorine Standard Addition Curve of NIST 1635 Coal Standard

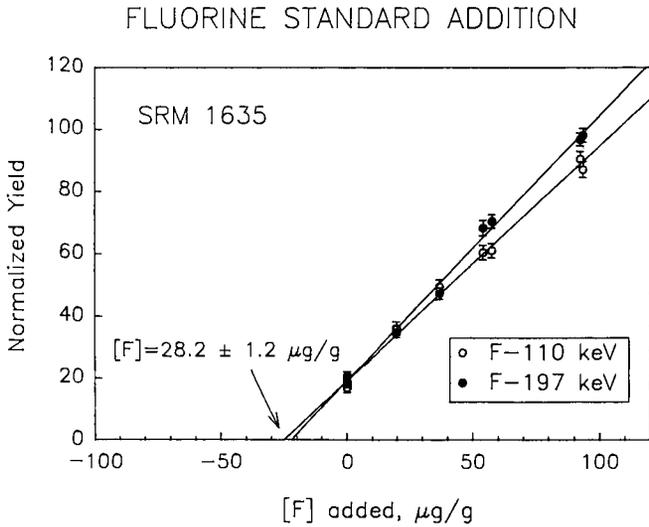


FIGURE II
Fluorine Standard Addition Curve of NIST 1632b Coal Standard

