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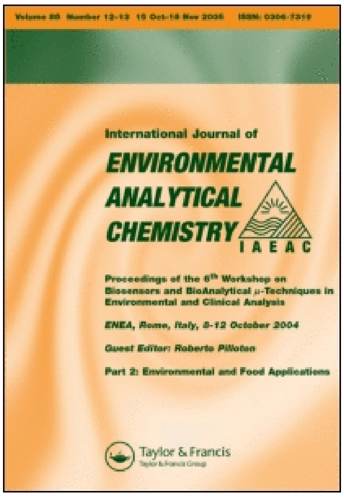

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Determination of Arsenic(III) and Arsenic(V) in Coal and Oil Fly Ashes†

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Total arsenic has been determined for fly ashes generated by conventional combustion of pulverized western coal, oil, a coal–oil mixture, a coal–water mixture, and from the fluidized-bed combustion of North Dakota lignite. For most of the ashes the total arsenic levels were between 100 and 200 ppm, but the coal–water mixture ash contained 348 ppm.

Leaching with 0.5 N H_2SO_4 or a pH 5 1 M citrate solution resulted in the removal of 78 to 97% of the total arsenic from the particles. This clearly indicates a high surface enrichment of arsenic on the particles, in agreement with numerous previous studies on coal fly ash.

The pH 5 citrate solution was more effective for the removal of arsenic from the particles without significant oxidative loss of arsenic(III). Speciation of arsenic in the citrate leachate by hydride atomic absorption spectrometry indicated that in most cases less than 2% of the soluble arsenic was arsenic(III). The only exception was the leachate of the coal–oil mixture ash, which contained about 7% arsenic(III). The actual arsenic(III) levels in the ashes never exceeded 6 μg per g of ash.

KEY WORDS: Arsenic, speciation, fly ash.

Several elements, such as As, Cr, Fe, and Se, can exist in environmental samples in more than one valence state. The biological activity of such elements can be highly dependent on their chemical form. Arsenic(III) is more toxic than arsenic(V).[1] Furthermore, epidemiologic data appear to indicate that inorganic

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arsenic(III) compounds represent a greater carcinogenic hazard than arsenic(V).[2,3] Thus the speciation of arsenic in environmental samples is an important issue.

Many workers have reported total arsenic concentrations in coal and oil fly ashes,[4-11] with values ranging from <100 ppm to 2000 ppm. Arsenic is one of several elements that are highly enriched on the surfaces of the fly ash particles,[8,11,12] so that it is readily available for leaching following deposition of ash particles in the lung. Surface techniques such as x-ray photoelectron spectroscopy and Auger electron spectroscopy lack the sensitivity to study arsenic at the levels found in most fly ashes. This paper addresses the dual problems of leaching the arsenic from the fly ash surface without altering the distribution of arsenic(III) and arsenic(V) and then quantitating the concentration of each oxidation state in the leachate.

Arsenic can be analyzed by several wet-chemical colorimetric procedures. The chemistry of As^{5+} as AsO_4^{3-} ion is similar to PO_4^{3-}, and in fact PO_4^{3-} as well as soluble silica interfere with the general molybdenum blue analysis of AsO_4^{3-}.[13-15] In general, fly ashes contain large quantities of silicon and the concentration of PO_4^{3-} is greater than or similar to the concentration of arsenic.[10] Even when corrections are made for these interferences, the As speciation is estimated by the difference in absorbance between two samples, one with and one without an oxidation or reduction step to convert all the arsenic to a single oxidation state.[14-16] Even though the sensitivity of the colorimetric method is $\sim 0.013\,\mu g$ As/ml at 1% absorption,[13] the interferences and our observation of oxidation of low levels of AsO_2^{1-} in the presence of high ratios of AsO_4^{3-} led us to abandon colorimetric methods.

Arsenic speciation or general total analysis by hydride generation using atomic absorption spectroscopy (AAS) offers two great advantages. Arsenic by hydride generation has a sensitivity of ~ 1 ng for 1% absorption,[17] which is comparable to the 5 ng sensitivity of interference-free As analysis by instrumental neutron activation analysis (INAA).[18] More importantly, arsenic is separated from the matrix as arsines of As^{3+} or As^{5+}. Since AAS is highly specific, only other hydrides (such as Sb, Sn, Se, Te, Bi, and Pb) can directly interfere, although high concentrations of Cu, Mn or Ni can suppress arsine generation prior to analysis.[19-21]

Several researchers[19–25] have shown that As^{5+} hydride generation is severely inhibited from solutions more basic than ~pH 4.0 when using $NaBH_4$ as the reductant. Conversely, As^{3+} generation is unimpaired under these conditions, which allows for As speciation by AAS. This obviates the need for the liquid nitrogen traps used by Braman *et al.*,[23] but requires two analyses; one for As^{3+} and one for total As. The procedure reported below has been applied to the speciation of As in coal and oil fly ashes.

EXPERIMENTAL

Reagents

All reagents used were analytical reagent or redistilled grade. The reductant was 3% (w/v) $NaBH_4$ (Aldrich Chem. Co., Milwaukee, WI) in 1% (w/v) NaOH. This solution was vacuum filtered through a 115 mL 0.2 μm filter unit (Nalge Co., Rochester, NY). The unit was vacuum washed (1:50 nitric acid:DD-water) and rinsed with double distilled water (DD-H_2O). After filtration of 200 mL of reductant the unit was cleaned again to dissolve insoluble carbonates and restore the initial filtration flow rate. Five hundred mL batches of reductant were stored in polyethylene bottles under refrigeration and could be retained for several weeks. Pressure was relieved once a week by temporarily loosening the cap.

Ash samples

The National Bureau of Standards (NBS) ashes certified for As were 1633, a blend of electrostatic precipitator (ESP) and mechanical collector coal fly ashes from five power plants and 1633A, an ash from a single coal-fired power plant. Stack coal fly ash (SCA) was aerodynamically fractionated *in situ* from the stack breeching after the ESP from a large Western coal-fired power plant burning low sulfur (0.5%), high ash (20%) coal.[26–28] Hopper coal fly ash (HCA) was reaerosolized ESP hopper ash from the same power plant that has been size-classified to remove most particles greater than 3 μm.[28, 29] The oil ash was from an ESP hopper of a commercial oil-fired power plant in southern California. COM[30] and CWM were baghouse ashes generated from the experimental burning of coal–oil and coal–water mixtures at the Pittsburg Energy Technology Center. FBC was baghouse ash from the combustion of lignite in an atmospheric fluidized bed combustor at the Grand Forks Energy Technology Center.[31]

Arsenic measurement

Arsenic was measured at 193.7 nm with a Perkin-Elmer Model 306 atomic absorption spectrophotometer equipped with a Mercury/Hydride System (MHS-10) and a Hewlett-Packard-7100B strip chart recorder. The As source was an electrodeless discharge lamp operated at 8 watts and 0.7 nm spectral bandwidth (slit 4). Acetylene and air flow rates were 2.5 and 11.5 L/min respectively using the 10 cm single slot burner head. Nitrogen was used to purge the MHS-10 system (2.5 kg/cm^2).

A 1000 μg As^{3+}/mL standard was prepared by dissolving 1.3204 g primary standard As_2O_3 (Mallinkrodt, St. Louis, MO) with 0.75 g NaOH as pellets in a minimum volume of DD-H_2O ($\sim$10–15 mL). The standard was diluted to $\sim$500 mL and 5 drops of phenolphthalein solution was added followed by the addition of 1 mL of 20 N H_2SO_4 to neutralize the excess NaOH. The solution was diluted to 1000 mL and stored in a polyethylene bottle. Working As^{5+} standards were prepared from dilutions of a commercial 1000 μg As^{5+}/mL stock as Na_2HAsO_4 in water (Varian Techtron, Palo Alto, CA).

For analysis of total arsenic, aliquots of the appropriate solutions were mixed in the polyethylene hydride reaction tubes with 10 mL of 0.5 M H_2SO_4 containing 1 μL of a saturated $KMnO_4$ solution to oxidize all arsenic to arsenic(V). Evolution of arsine from arsenic(V) solutions at pH $>$4.0 is very low.[19–25] Therefore, arsenic(III) was measured in a matrix of 10 mL of 1.0 M sodium citrate at pH 5.0. The determination of small concentrations of arsenic(III) in the presence of high concentrations of arsenic(V) requires a signal correction. A standard curve for arsenic(V) in the pH 5.0 sodium citrate matrix was prepared. Since the total arsenic concentration was measured as described above, the signal from the pH 5.0 solutions could be partitioned between arsenic(III) and arsenic(V). For samples with less than 100 ng arsenic(V), no correction was necessary.

Fly ash extractions

For measurement of total acid-soluble arsenic, duplicate fly ash samples (0.2–0.9 g) were suspended in 50 ml of 0.5 N H_2SO_4 and mechanically shaken overnight. The suspension was centrifuged and 10–40 μL aliquots of the supernatant were taken for analysis.

For the measurement of arsenic(III), duplicate ash samples (250–1250 mg) and a third ash sample spiked with 25 μL of 1000 μg/mL arsenic(III) standard were all dried overnight at 60°C. 50 mL of 1 M sodium citrate at pH 5.0 were added to each sample, and the ash suspensions were shaken overnight. The suspensions were vacuum filtered through 47 mm, 0.2 μm Nuclepore filters, and the filtrate was analyzed for arsenic(III). The undissolved residue was liberally washed with distilled water and dried at 60°C overnight. This ash was then suspended in 50.0 mL of 0.5 N H_2SO_4 and shaken overnight. The suspensions were centrifuged, and 50–250 μL aliquots of the supernatant were taken for analysis of total arsenic.

Total digestion

Ashes NBS-1633, HCA and SCA were digested using the procedure of Silberman and Fisher.[26] The other ashes followed the technique outlined by Harris *et al.*[30] The difference between the two techniques is the recent use of 6 M HCl to initially extract the ash prior to the addition of HF and the use of a low temperature ashes (LTA) to oxidize the residual unburned carbon content of oil ash, CWM, COM, NBS-1633A, and FBC ashes.

Total As by INAA

Analyses of the stack-collected coal ash (SCA) and the coal hopper ash (HCA) have been previously reported.[8,28] The oil ash and COM ash were analyzed by Dr. R. H. Filby at Washington State University according to published procedures.[32] The FBC and CWM ashes were analyzed by L. E. Kovar at General Activation Analysis, Inc. (San Diego, CA).

RESULTS

Initially 0.5 N H_2SO_4 and 0.1 N NaOH were chosen as probable extractants of As from fly ash surfaces based on the work of Johnson and Barnard.[33] They showed that these extractants were superior to 0.5 N HCl for removing As from four western N.Y. soils. We found that 0.5 N H_2SO_4 was far more effective in removing As from the coal hopper fly ash than was 0.1 M NaOH. Therefore, the H_2SO_4 was used for subsequent leaching studies.

The arsenic in coal fly ashes is generally considered to be accessible to leaching solvent because of its high surface enrichment.[4,7–9,11,12,34] Total arsenic was measured both for H_2SO_4 leachates and for totally digested ash samples. The ratio of the two measured arsenic concentrations gives the percent recovery of arsenic by acid extraction as shown in Table I.

TABLE I

Total arsenic and percent recovery by leaching with 0.5 N H_2SO_4.

Ash	Total arsenic[a] (HF digestion)	Total arsenic[a] (INAA)	0.5 N H_2SO_4[a] leachate	Percent recovery
Oil ash	71.5 ± 2.2	97 ± 12	57.1 ± 6.9	80 ± 10
SCA	148 ± 7	132 ± 22[b]	116 ± 6	78 ± 4
HCA	190 ± 5	188 ± 22[c]	172 ± 7	91 ± 4
NBS-1633A	143 ± 8	145 ± 15	126 ± 1	88 ± 5
CWM	nd[d]	348 ± 8	313 ± 7	90 ± 2
COM	109 ± 1	103 ± 1	91 ± 11	83 ± 10
FBC	104 ± 9	86 ± 4	101 ± 10	97 ± 10
NBS-1633	64	61 ± 6	55 ± 3	86 ± 5

[a] Values represent μg As per g of ash.
[b] Value from reference 6.
[c] Value from reference 27.
[d] Not determined.

Although 0.5 N H_2SO_4 was an effective leaching agent for arsenic in fly ash, the highly acidic conditions resulted in the oxidation of arsenic(III) in the samples, as determined by studies in which arsenic(III) was added to the fly ash samples. Using less concentrated H_2SO_4 to prevent the oxidation of arsenic(III) diminished the percent recovery of arsenic from the ash. However, this decrease in arsenic recovery could be largely restored by the use of 1.0 M sodium citrate as the leaching agent. Furthermore, the use of pH 5.0 1.0 M sodium citrate provided excellent recovery of spiked arsenic(III) as shown in Table II. The only significant losses of arsenic(III) were associated with the fluidized bed lignite ash. The agents responsible for this loss of arsenic(III) have not been identified.

TABLE II

Recovery of 25 μg arsenic(III) added to fly ash samples.

Ash	% Recovery
Oil ash	99
SCA	98
HCA	105
NBS-1633A	100
CWM	100
COM	109
FBC	70
NBS-1633	96

Samples of each fly ash were leached first with pH 5.0, 1.0 M sodium citrate, then with 0.5 N H_2SO_4. The citrate leachate was analyzed for arsenic(III) and total arsenic. The H_2SO_4 leachate was analyzed for only total arsenic. The results are shown in Table III. The sequential citrate/H_2SO_4 leaching produced essentially the same value of total arsenic as does the 24 hr H_2SO_4 leaching shown in

TABLE III

Analyses of arsenic(III) and total leachable arsenic from fly ash.[a]

	Citrate leachate				Citrate
Ash	As(III)	As(V)	H_2SO_4 leachate	Total arsenic	total (%)
Oil ash	0.5	45.1	15.1	60.7	75
SCA	2.5	115	3.6	121	97
HCA	0	143	15.7	159	90
NBS-1633A	0.6	115	11.3	127	91
CWM	3.0	300	27.7	330	92
COM	5.6	75	8.2	80.8	91
FBC	0	102	2.8	105	97
NBS-1633	0.5	51.4	3.2	55.1	94

[a] All concentrations in units of μg As per g of ash.

Table I. Except for the oil ash the citrate alone leaches $\geqq 90\%$ of the acid soluble arsenic. The concentrations of arsenic(III) are quite low, ranging from zero to highs of 3.0 and 5.6 μg/g ash for the CWM and COM ashes, respectively.

DISCUSSION

Arsenic is known to be associated with the mineral matter in coal[34] especially in the greater than 2.79 g/cm^3 density sink fraction which is represented by some of the heavier oxides, sulfides or sulfates. Theis and Wirth[7] showed that arsenic was associated with Fe in 9 coal fly ashes, though in one ash sample As appeared to be associated with Al. The 0.5 N H_2SO_4 solubilized an average of 87% of the total As present (Table I). Several other workers have reported similar values for the percent of acid-extractable arsenic.[6,7,9,11] Dressen *et al.*[6] extracted 64% in 1.0 M HNO_3, 78% in 1.0 M HCl, and 59% in 0.1 M citric acid. Hansen and Fisher[11] reported an average extraction of 98% from 0.21–0.57 M HCl. Theis and Wirth[7] estimated that 93% of As is associated with the surface of fly ash. It has been reported that 10–15% of the arsenic in coal is associated with the acid-insoluble silicates.[34] When the silicates are dissolved by HF, complete recovery of the arsenic in the fly ash is obtained, as shown by the generally good agreement between the total arsenic values by HF digestion and neutron activation (Table I).

The reported association of arsenic with iron and aluminum compounds[7] led to our choice of citrate as a leaching agent for arsenic. Although citrate is not expected to react directly with either arsenite or arsenate, it has been shown to dissolve large amounts of iron and aluminum compounds from fly ash surfaces,[35] thus freeing matrix-bound arsenic. There was no attempt to extract ash with highly acidic citrate solutions. Even though recoveries may have been improved, the presence of high concentrations of uncomplexed Fe^{3+} could lead to oxidation of solubilized As^{3+}. Solutions at pH 6 and pH 9 used by Theis and Wirth[7] in extracting As from ash samples and extractions using distilled H_2O, saturated H_3BO_3 and 0.1 M pH 7.4 tris buffer[9] were all less effective in recovering known As concentrations.

The speciation of arsenic was complicated by the oxidation of arsenic(III) in strongly acidic leaching solutions. This problem was solved by the use of the citrate buffered at pH 5.0, which was able to effect satisfactory recovery of arsenic under mildly acidic conditions. There is in fact relatively little arsenic(III) in any of the ashes included in this study. The highest concentration was 5.6 μg As/g ash for the COM ash. This does not appear to be necessarily typical of oil-based fuels, since the oil hopper ash contained only 0.5 μg/g ash. The CWM ash had 3.0 μg As(III)/g ash, but because of the high total arsenic content of this ash, this value represents $<1\%$ of the total arsenic.

Turner has reported analyses of ash pond effluents in which 2 to 40% of the dissolved arsenic was arsenic(III).[36] He also conducted laboratory leaching studies using distilled water as the solvent and found as much as 65% of the dissolved arsenic as arsenic(III). However, in the laboratory studies only 0.03 to 16% of the total arsenic was solubilized, and the highest fractions of arsenic(III) were found when very small percentages (0.03–0.8%) of the total arsenic was dissolved. Our results indicate that most ashes probably have a relatively small percentage of total arsenic as arsenic(III). Thus the high fraction of arsenic(III) observed by Turner[36] when only a small percentage of the total arsenic is leached may be due to a higher solubility of the arsenic(III) species in the ash.

The FBC ash was unique in that we observed only 70% recovery of arsenic(III) which was added to the ash. This ash presumably contains acid-soluble species capable of oxidizing arsenic(III) to arsenic(V), since we could obtain a complete recovery of total arsenic. Since we have only one fluidized bed ash, we cannot determine whether this type of behavior is typical of FBC ashes.

The greatest uncertainty in the determination of arsenic(III) is the lack of complete leaching of acid-soluble arsenic by the citrate solution. It is possible that arsenic(III) is enriched in the small pool of arsenic that is not leached by citrate. However, this seems unlikely, and with the exception of the oil ash, the maximum amount of arsenic(III) would still be $\leq 15\%$ of the acid-soluble arsenic.

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