

Extractable Arsenic and Antimony in Activated Carbons

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Summary: With activated carbon such a conspicuous component in the POU/POE industry, many water treatment dealers take its safety and efficacy for granted. One company set out to test this theory. The results, taken over a two-year study, may surprise you.

Several years ago, a comprehensive study of the activated carbon industry showed arsenic and antimony contamination in activated carbon products. Continuous and comprehensive testing of activated carbon for extractable toxic elements appears to be the only available means to ensure the reliable purity of received activated carbons, and members of the POU/POE industry were urged to institute appropriate controls.

Activated carbons are broadly used in POU/POE devices as well as many municipal-scale, potable water treatment systems. These activated carbons are usually derived from various types of coal (i.e., anthracite, bituminous, lignite) or natural materials such as wood and coconut shell. There have been concerns about the amount of naturally present arsenic, antimony and aluminum that can be extracted from these materials when used to produce potable water. With revision of the U.S. Environmental Protection Agency (USEPA) arsenic standard in potable water from 50 parts per billion (ppb) to 10 ppb, many users may not be aware of the extent of these extraction problems and their possible impact on selecting activated carbons for use in POU/POE applications.

To help understand the extent of the toxic trace element problem in activated carbons, a multi-year study of the extractable amounts of arsenic, antimony and aluminum in activated carbons sold for use in POU/POE applications was initiated. With results for more than two years, this article reports only on the arsenic and antimony results of that study, as extractable aluminum can be controlled by most manufacturers through use of basic, acid-washing procedures.

Gathering test subjects

A broad range of activated carbons (39 grades from 19 manufacturers) were obtained for the study. Coal-based carbons were, in almost all cases, acid-washed, while coconut-shell carbons were mostly water rinsed. Each was selected by the manufacturer to represent its best available carbon

containing the lowest possible extractables. Hence, the samples received were all used in the POU/POE industry, many being NSF Standard 61 or 42 registered. It's important to point out that a less careful selection of grades for testing would have potentially demonstrated a much more severe extractable arsenic and antimony problem.

In a second part of the study, two grades of coal-based activated carbon were selected—one from a domestic source and the second from an off-shore source—and a total of 1,600 trace element extraction assays were performed for individual production lots (usually 10,000 to 44,000 pounds of activated carbon in each lot) over more than two years.

Table 1. Summary of activated Carbon extractions for best available commercial Products

Manufacturer/product (Number of samples tested)	Carbon source	Highest Arsenic (PPb)	Highest Antimony (PPb)
1A (15)	Bituminous Coal	7.5	4.2
18 (5)	Coconut Shell	26	2
2A(2)	Bituminous Coal	182	22
3A (14)	Bituminous Coal	61	16
3B(2)	Bituminous Coal	5	14
3C(2)	Bituminous Coal	N.D.	N.D.
4A(1)	Bituminous Coal	5	3
6A(2)	Bituminous Coal	8	30
7A(6)	Bituminous Coal	21	3
7B(3)	Coconut Shell	N.D.	N.D.
8A(6)	Bituminous Coal	16	20
9A(2)	Bituminous Coal	13	4
9B(2)	Bituminous Coal	65	7
9C(3)	Bituminous Coal	65	13
10A(1)	Bituminous Coal	212	23
11A (1)	Bituminous Coal	18	10
11B (2)	Coconut Shell	N.D.	N.D.
11C(1)	Coconut Shell	5	N.D.
11D (2)	Coconut Shell	N.D.	N.D.
11E(1)	Coconut Shell	N.D.	N.D.
12A (5)	Bituminous Coal	189	62
13A (2)	Bituminous Coal	N.D.	N.D.
13B (25)	Coconut Shell	13	N.D.
13C (18)	Coconut Shell	7.4	N.D.
14A (2)	Bituminous Coal	8	N.D.
15A (4)	Coconut Shell	N.D.	N.D.
15B (1)	Coconut Shell	N.D.	N.D.
15C (2)	Coconut Shell	4	N.D.
15D (4)	Bituminous Coal	11	N.D.
15E(1)	Bituminous Coal	N.D.	N.D.
16A (1)	Coconut Shell	N.D.	N.D.
16B (1)	Coconut Shell	7	N.D.
17A(1)	Coconut Shell	N.D.	N.D.
18A (1)	Coconut Shell	6	N.D.
18B (1)	Coconut Shell	471	167
18C (1)	Coconut Shell	N.D.	2.4
18D (1)	Coconut Shell	6	3
19A (2)	Coconut Shell	73	3
20A(1)	Bituminous Coal	N.D.	N.D.

N.D. = non-detect.
Numbers in red exceed current USEPA standards by greater than 50%.

The number of tests ranged from no less than three samples per lot up to a maximum of 10 tests from different 1,000-pound bags within the same lot. During this systematic and long-term study, the goal was to see if these world-class manufacturers of activated carbon could sustain extractables below current USEPA requirements.

A different approach

The extraction assay method represents the NSF Standard 42 procedure generally applied during the late 1990s (see *FYI: Details*). NSF Standard 42 extraction protocol has been amended over the years, and today this method differs from the method applied in this study; however, the goal was to observe how activated carbon purity varied over an extensive period of time using a single consistent method of analysis.

Table 1 shows the test results on the different high-purity grades of activated carbon sold within the POU/POE industry. As indicated, some carbons didn't meet current NSF or USEPA standards for either arsenic (10 ppb) or antimony (6 ppb) during a 72-hour extraction test. What's alarming about these results is that a high percentage of coal-based activated carbons (those supplied by 12 out of 15 manufacturers) didn't meet current standards, and seven manufacturers supplied product five times the limit or higher for at least one toxic element. In effect, the probability that one can purchase coal-based activated carbon that is low in toxic extractables is very poor.

Cracking the shell

Many people think coconut shell carbons are intrinsically less likely to display high concentrations of extractables. Four out of nine manufacturers of coconut shell activated carbon, however, did not meet the arsenic standard. In some cases, extractable levels of arsenic and antimony rose to very high levels (one coconut shell-based carbon product contained levels that would potentially represent an immediate acute toxic hazard). Additional studies have shown no correlation between extractable arsenic and antimony and other properties of these products. In addition, bulk elemental assays by such methods as X-ray fluorescence have shown no correlation to the quantity of elemental arsenic or antimony that is extractable from these samples. Because of the extremely poor results listed here, one should be concerned about those users who specify activated carbon that isn't acid-washed or selected for purity. These grades make their way in large volumes into both the POU/POE industry and in even higher volumes into the municipal water treatment market.

Next, two grades of coal-based activated carbon were selected for much more detailed and long-term analysis. Both grades were 12 x 40 mesh, nominal 1,000 square meter per gram BET surface area (as determined by nitrogen adsorption), acid-washed, bituminous coal-based carbons that were pulverized and then re-agglomerated and purchased on the same specification. These grades were chosen as representing the best state-of-the-art materials available to the POU/POE industry for routine applications.

Figures 1 and 2 summarize arsenic and antimony concentrations measured for Vendor 13, Grade D over this period. Five production lots exceeded arsenic standards, but only one lot by a significant amount. But, extractable antimony exceeded targets approximately 70 times, although only five times by a factor of two. Figures 3 and 4 summarize arsenic and antimony concentrations measured for Vendor 1, Grade A. Extractable arsenic exceeded limits approximately 37 times, but in no case by more than a factor of 50 percent. No sample contained extractable antimony above the required limit.

These results demonstrate that even exceptional suppliers have their bad days. In the case of Vendor 13, antimony problems occurred annually during springtime following a planned maintenance period, and there wasn't a successful diagnosis of why this

Figure 1. Vendor 13, Grade D extractable arsenic

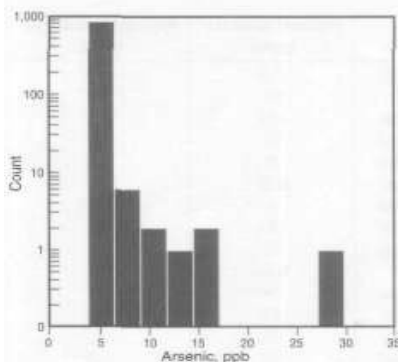
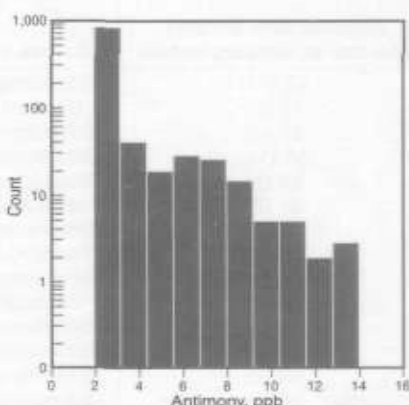


Figure 2. Vendor 13, Grade D extractable antimony



FYI: Details of analytical and sampling methods

For this study of activated carbon extractables, samples of commercial, bituminous coal-based activated carbons were obtained by requesting a 12 x 40 or 20 x 50 mesh activated carbon of about 900-1,100 square meters/gram BET surface area and having the lowest practicable trace metals (arsenic, antimony and aluminum) content. Alternatively, the instructions were to provide a coconut shell-based activated carbon with a BET surface area or iodine number of 1,000-1,250 and, when possible, in water-washed or acid-washed form. Mesh size of the carbons varied from 20 X 50 to 80 x 325 mesh. These specifications were selected to represent the most common grades used in the production of POU/POE devices for either chlorine or volatile organic compounds/total trihalomethane (VOC/THM) reduction. The complete specifications also included allowed ranges for total ash, water soluble ash, hardness and other parameters commonly used in the purchase of activated carbons. Each sample provided by the manufacturers was analyzed for all specification parameters to determine if the samples were of commercial quality, and no manufacturer failed to produce samples meeting routine quality control screening.

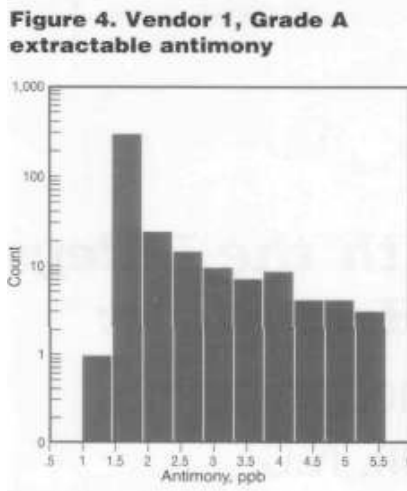
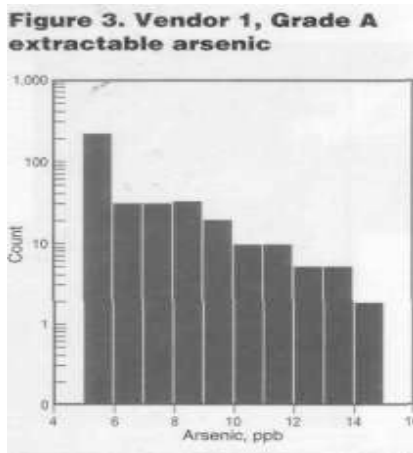
A five-gram sample of the received activated carbon was placed into a clean 50 milliliter (ml) Teflon beaker with 20 ml of deionized (D1) water (minimum 5 megohm). A 20 ml DI water sample in an empty Teflon beaker was used as a control blank. The sample was stirred, then covered and allowed to sit at room temperature for 72 hours. The sample was then decanted and filtered through a 0.2 micrometer, LuerLock syringe membrane filter. The supernatant was then analyzed using a multi-tube Perkin-Elmer graphite boat atomic adsorption spectrophotometer with automatic sampling, matrix modifier, blank and calibration capabilities. All standards and reagents were analytical grade and/or NIST traceable.

While NSF later amended its procedure to a triple extraction of a sample with 24-hour intervals between sampling, the testing in this report retained the original 72-hour extraction procedure to avoid a change in analytical methods in the middle of the study. It should be recognized that the 72-hour extraction produces a more rigorous outcome than the amended triple 24-hour extraction, and the results reported here may represent a more aggressive extraction than would be obtained with the amended ANSI/NSF procedure. Side-by-side comparison of the two extraction procedures demonstrates a roughly 50 percent lower concentration in the new ANSI/NSF standard than in the original procedure. As such, results measured using the 72-hour extraction, and no more than 50 percent above the current USEPA limit, are considered likely to pass the new ANSI/NSF standard.

happened. Vendor 1 demonstrated a completely random pattern of extractable arsenic and antimony concentrations, i.e., problems occurred infrequently, not to a severe degree, and without a discernable pattern.

These results demonstrate that limited testing or certification of activated carbons based upon a small statistical sample—as currently applied by ANSI/NSF procedures—isn't likely to provide accurate guidance on product quality and sustainable control of arsenic and antimony extractables from POU/POE activated carbons, even with the best manufacturers and their best available grades. Only a small fraction of current manufacturers have the means to produce clean product with low extractable arsenic or antimony. In fact, only a handful of coal-based activated carbon producers can meet these standards on a continuous basis.

Although outside the scope of research, these results indicate that the use of bituminous coal-based activated carbons—not acid-washed or otherwise treated to provide low levels of extractable arsenic and antimony—represent a significant and unrecognized problem for municipal water treatment facilities. This is because it is unlikely that you'll observe methodical monitoring of these extractables during start-up of large municipal carbon beds; and, in some cases, extensive rinse-up of the beds would be required to drive concentrations down to low values.



Continuous and comprehensive testing of activated carbon for extractable toxic elements appears to be the only available means to ensure the reliable purity of received activated carbons, and members of the POU/POE industry are urged to institute appropriate controls. In 2000, a TSCA Section 8(e) report was filed with the USEPA regarding these problems. This filing served to shield the point-of-use/point-of-entry (POU/POE) water treatment industry from liability and prosecution under the Toxic Substances Control Act for distribution of products known to expose users to a hazardous chemical. As a result of this filing, the most severe potential penalties for use of contaminated activated carbons have been mitigated for the entire industry; but this filing does not provide a shield against legal prosecution under state statutes such as California Proposition 65.

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