

ELEMENTAL ANALYSIS OF GRAPHITE

H. K. Mayer

UCAR Carbon Company Inc.

12900 Snow Road, Parma, OH 44130 USA

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Introduction

The elemental analysis of graphite has become more important in recent years as customers in the nuclear, semiconductor, and metals processing industries have realized how specific impurities affect their processes. These customers have demanded more accurate analyses at lower detection limits. Impurities in the final graphite product result from elements present in the coke and pitch used as raw materials and from processing. A significant portion of the impurities is removed at graphitization temperatures, but complete removal generally requires an additional purification step.

No single method is preferred for the elemental analysis of graphite. ASTM Test Method C560 describes methods for the wet chemical analysis of silicon, iron, calcium, aluminum, titanium, vanadium, and boron; however, with the exception of boron, these methods are now rarely used due to the time involved. Instrumental analysis techniques are preferred currently. Choice of an instrumental technique depends on elemental capability, detection limit required, cost of analysis, analysis time, and confidence in results (quantitative vs. semi-quantitative analysis).

Instrumental techniques commonly used for the analysis of graphite include x-ray fluorescence spectroscopy (XRF), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), direct current arc-optical emission spectroscopy (DCA-OES), glow discharge mass spectrometry (GD-MS), and spark source mass spectrometry (SS-MS). XRF has the advantage of simple sample preparation, but requires matrix-matched standards. GD-MS and SS-MS also have the advantage of solid sampling, but require high-quality reference materials and the instruments are expensive to purchase and maintain. There are very limited sources of certified graphite reference materials available [1], and none are available for high-purity graphite. ICP-AES can be used to analyze graphites of varying purity levels with reasonable accuracy, and graphite reference materials are not required. Disadvantages of ICP-AES include loss of elements in the ashing step (e. g., phosphorus and sulfur) and the amount of time required for sample preparation. In order to illustrate these points, comparative elemental analysis data

were obtained by applying several instrumental techniques to production carbon and graphite materials.

Experimental

The samples analyzed by ICP-AES were ashed in platinum dishes in a muffle furnace. The resulting ash was fused with lithium metaborate and then dissolved in dilute nitric acid. The solution was analyzed using a Spectroflame simultaneous/sequential ICP-AES. Samples with low ash content were blank subtracted.

XRF data were obtained from milled graphite samples using a KeveX 771 energy dispersive x-ray fluorescence spectrometer (ED-XRF). DCA-OES measurements were performed on an ARL 3560. GD-MS data were obtained from Shiva Technologies, Syracuse, NY. SS-MS data were obtained from Northern Analytical, Merrimack, NH.

Results and Discussion

A comparison of elemental analysis results for carbon electrodes, obtained by means of ICP-AES and XRF, is shown in Table 1. ICP-AES has been the method of choice for elemental analysis due to its accuracy. However, for matrices that have well-characterized reference materials available, XRF is also an acceptable technique, as shown by the ratios in Table 1.

Graphite electrodes have much lower impurity levels than carbon electrodes due to the higher temperature involved in processing. Several techniques were used to analyze a graphite electrode (see Table 2). ICP-AES has the best recovery of elements as compared to ash content (assuming that ash is comprised of elemental oxides). XRF has comparable recoveries. GD-MS and SS-MS techniques give poor results for this level of impurities in graphite.

Purified graphites provide a challenge for any instrumental analysis technique because the elemental impurities are near the detection limits. A comparison of the elemental analyses of purified graphite using ICP-AES, GD-MS, and DCA-OES is shown in Table 3. ED-XRF is not suitable due to its high detection limits. The SS-MS technique was not used because it does not differentiate purified and unpurified graphites. DCA-OES can distinguish between

purified and unpurified materials, but does not have the detection limits required for current purification levels. ICP-AES and GD-MS have both the detection limits and accuracy for purified graphites, and give similar results.

Conclusions

XRF and ICP-AES have been shown to be suitable analysis techniques for carbon and graphite. For purified graphites, ICP-AES or GD-MS techniques are recommended.

Acknowledgments

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Reference

- [1] Boegershausen, W, *et al.* Fresenius J Anal Chem 1997;357(3):266-273.

Table 1: Analysis of a Typical Carbon Electrode

Element	XRF (ppm)	ICP-AES (ppm)	Ratio (XRF/ICP) (ppm)
Na	ND	230	ND
Mg	ND	380	ND
Al	6900	9500	0.73
Si	10300	12400	0.83
P	<38	ND	ND
Cl	48	ND	ND
K	1100	910	1.2
Ca	1200	700	1.7
Ti	910	730	1.2
V	29	21	1.4
Cr	27	11	2.4
Mn	20	15	1.3
Fe	2600	2100	1.2
Ni	17	<0.6	ND
Cu	200	120	1.7
Zn	12	20	0.6
Sr	73	72	1.0
Y	<7	ND	ND
Zr	23	23	1.0
Ba	ND	110	ND
Pb	<20	ND	ND
Recovery	82%	102%	--

ND = Not Determined

Table 2: Analysis of a Typical Graphite Electrode

Element	XRF (ppm)	ICP-AES (ppm)	GD-MS (ppm)	SS-MS (ppm)
Na	ND	<1	1.8	3
Mg	ND	0.1	<0.05	0.5
Al	<165	18	11	7
Si	<37	3.0	5	2
P	<38	ND	<0.01	0.5
Cl	<10	ND	5	6
K	<9	3.7	1.7	1
Ca	130	130	60	67
Ti	13	11	2	1
V	9	5.2	1.5	0.1
Cr	2	0.8	2	0.4
Mn	<6	0.7	<0.005	0.1
Fe	1770	1700	600	3
Ni	19	22	8	0.2
Cu	<2	<0.06	0.2	0.2
Zn	<4	0.4	<0.05	0.3
Sr	<7	1	0.2	0.2
Y	<7	ND	<0.05	0.1
Zr	<7	0.3	<0.01	<0.2
Ba	ND	2.1	0.5	2
Pb	<20	ND	<0.01	<0.1
Recovery	93%	91%	33%	4%

Table 3: Analysis of a Typical Purified Graphite

Element	ICP-AES (ppm)	GD-MS (ppm)	DCA-OES (ppm)
B	ND	0.2	<0.2
Na	<0.2	0.2	<0.2
Mg	<0.01	<0.05	<0.2
Al	<0.2	0.2	<0.2
Si	<0.2	0.5	<0.2
K	<1.7	<0.05	<0.2
Ca	<0.07	0.2	<0.2
Ti	<0.04	0.01	<0.2
V	<0.01	<0.005	<0.2
Cr	<0.04	<0.1	<0.2
Mn	<0.02	<0.005	<0.2
Fe	0.1	0.07	0.2
Ni	<0.04	0.02	<0.2
Cu	<0.01	<0.05	<0.2
Zn	<0.01	<0.05	<0.2
Sr	<0.01	<0.01	ND
Mo	<0.04	<0.01	ND
As	ND	<0.1	<0.2
Sn	ND	<0.01	<0.2
Sb	ND	<0.01	<0.2