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Yield and Pore-size Distribution of Pyrolysis Products of Organic Compounds as Chemical Modifiers in Electrothermal Graphite Furnace Atomic Absorption Spectrometry†

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Yields of pyrolysis products and pore-size distribution of amorphous carbon produced from organic chemical modifiers, such as ascorbic acid, glucose and sucrose, for electrothermal atomization atomic absorption spectrometry were examined: the pyrolysis yield (for which ascorbic acid > glucose > sucrose) and the pore-size distribution are independent of the modifier used.

Organic compounds have been used as chemical modifiers for elements such as lead,[1–6] tin,[6,7] antimony,[8] selenium,[8] indium,[9] gallium[10] and gold[11–14] in graphite furnace atomic absorption spectrometry (GFAAS). The effectiveness of organic compounds has been discussed from viewpoints of the formation of active carbon species and reductive gases. In previous work pyrolysis processes have been reported for (i) gaseous compounds (hydrocarbons, CO and CO_2) below 580 K; (ii) active carbon species such as soot between 600 and 1100 K; and (iii) thermally stable carbon species between 1200 and 2400 K.[15] The thermally stable carbon species was assigned to amorphous carbon by Raman spectrometry.[15] Recently, it was suggested that the effectiveness of an organic chemical modifier for indium is due to the proportion of the surface area coated by the amorphous carbon and absorption into the micro-sized pores in the amorphous carbon.[9] When discussing the degree of the effectiveness of organic chemical modifiers, it is useful to examine the pyrolysis yield and the pore-size distribution of the amorphous carbon. In the present work the pyrolysis yield and pore-size distribution for ascorbic acid, glucose and sucrose are reported and the effectiveness of ascorbic acid and sucrose on GFAAS for indium and gallium is discussed.

Experimental

A Hitachi model Z-8000 flame and graphite furnace atomic absorption spectrometer equipped with a Zeeman effect background corrector, an optical temperature controller system (Hitachi model 180–0341), an automatic sampler and an automatic data processor was used. The analytical wavelength and spectral bandwidth were 325.6 nm and 1.3 nm for indium and 294.3 nm and 0.4 nm for gallium, respectively. Temperature data were calibrated using a Chino model IR-AH1 S radiation thermometer. The thermometer was calibrated with a Pt–Rh thermocouple. The standard atomizer conditions are given in Table 1.

Raman spectra were measured at room temperature by means of a Jobin-Yvon Ramanor T64000 based on a triple 0.64 m focal length monochromator equipped with three 1800-grooves/mm gratings and a 1024×256 element CCD detector; a triple subtractive configuration and 3.5 cm^{-1} spectral bandwidth were used. For macroscopic measurements, the 514.5 nm line of an argon ion laser with a low power of 20 mW at the sample and 180 ° scattering was used to avoid thermal decomposition. The wavenumbers of the observed Raman spectra were calibrated using the argon plasma lines (514.5 nm).

Specific surface area and absorption pore-size distribution of amorphous carbon were obtained using a Shimadzu model ASAP-2000 with N_2 adsorption gas by BET and BJH methods, respectively.

Aliquots of a commercially available standard solution were diluted with 0.1 mol dm^{-3} nitric acid before use. Distilled and deionized water was purified with a Milli-Q Plus system.

Table 1 Standard atomization conditions

	Stage			
	Dry	Pyrolysis	Atomization[b]	Cleaning
Temp.[a] (T/°C)	120	varying	2800	2900
Ramp time (t/s)	30	20	0	0
Hold time (t/s)	0	10	3	3
Inner gas flow (ml m^{-1})	200	200	30	200

[a]Programmed for the atomizer unit. [b]An optical temperature controller was used.

Results and Discussion

A pyrolytic graphite-coated (PG) furnace was heated until a constant weight as measured by an analytical balance was reached. The organic matrix modifier (2 mg: 40 μl of 50 g l^{-1}) was pyrolysed with the furnace in the atomizer unit according to the standard atomizer conditions except for the atomization and cleaning stages (Table 1) and this process was repeated three times (6.0 mg of modifier pyrolysed). Then, the furnace was removed and weighed. A pyrolysis yield (%) was obtained from the equation [weight change in mg]/6.0 (mg) $\times$ 100. The detectable low limit and the uncertainty of yield were 2% for yields of 6.0 mg (0.1 mg of mass) and 2%, respectively. The yields at pyrolysis temperatures of 640 and 1230 K are shown in Table 2 with the standard deviation (n = 5). At 640 K, the yield increases in order sucrose < glucose < ascorbic acid. The weight loss of the compounds is attributed to a release of gaseous species, such as hydrocarbons, water and carbon monoxide. When the pyrolysis temperature was increased to 1230 K, the yield by weight decreased. Since active carbon species, such as soot, vaporize over the temperature range 970–1100 K,[11,15] the yield is attributed to that of amorphous carbon and the decrease in yield is attributed to the release of active carbon species. The pyrolysis yield for ascorbic

Table 2 Pyrolysis yield of 6.0 mg of organic chemical modifier in a PG furnace

Pyrolysis temperature (T/K)	Pyrolysis yield (%) (n = 5)		
	Ascorbic acid	Glucose	Sucrose
640	32 ± 3	7 ± 2	2 ± 2
1230	22 ± 2	2 ± 2	< 2

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acid is clearly more than approximately 10-fold that for glucose and sucrose.

After pyrolysis of 1.0 mg (20 μl of 50 g l^{-1}) of the organic chemical modifiers at 1000 K, Raman spectra at the centre

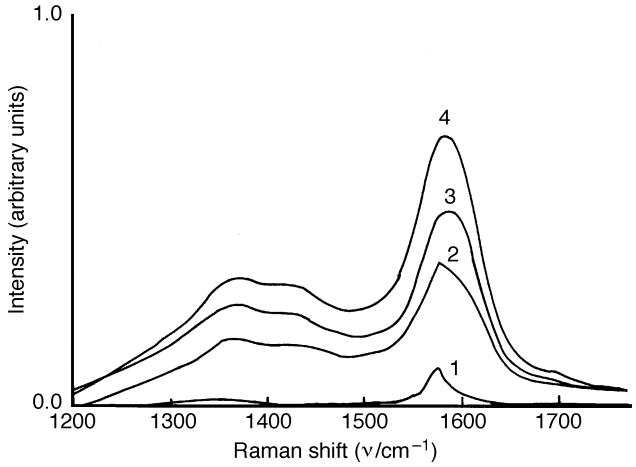

Fig. 1 Raman spectra of a surface of sample compartment of a PG furnace: 1, bare furnace; 2–4, after pyrolysis of 1 mg of organic matrix modifier at 1000 K: 2, sucrose; 3, glucose; 4, ascorbic acid

of the bottom of the sample compartment were observed through the sample injection hole of the furance with the bare PG furnace, as shown in Fig. 1. For the PG surface (line in Fig. 1), two Raman bands, a band corresponding to the E_{2g} mode near to 1584 cm^{-1} (G band) and a broad band for disorder mode with weak intensity of approximately 1361 cm^{-1} (D band) were observed.[16] After pyrolysis of the organic chemical modifier, the intensity near the positions of the G and D bands was increased with an increase in the intensity at the bottom between both bands. In the case of ascorbic acid the Raman shifts of the two broad bands were 1591 and 1381 cm^{-1}, respectively, and that for the shoulder was 1430 cm^{-1}. However, the broad bands cannot be assigned at the present time. For sucrose, the D band of the PG surface may form a sharp peak on the broad peak for the pyrolysis product. The intensity of the Raman band is due to the proportion of the surface area coated by the pyrolysis product relative to the area of the laser beam spot (100 μm diameter) at the centre of the bottom of the sample compartment. The order of the intensities, which is sucrose < glucose < ascorbic acid, is in agreement with that of the pyrolysis yield.

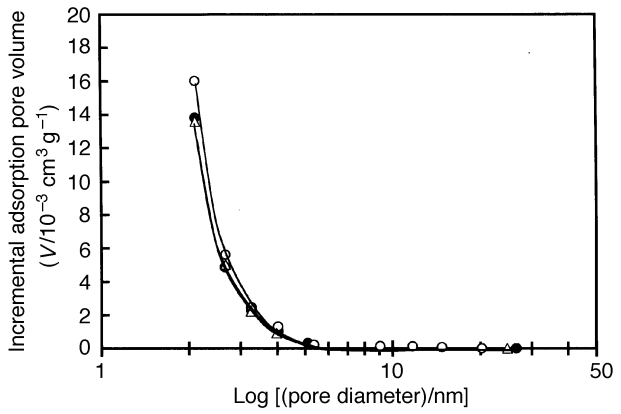

Fig. 2 Pore-size distribution of amorphous carbons pyrolysed at 1170 K: ●, ascorbic acid; ○, glucose, △, sucrose

Table 3 Effect of organic chemical modifier on the integrated absorbance for 2 ng of indium and gallium

Matrix modifier	Relative value of integrated absorbance	
	Indium	Gallium
Absent	1.00	1.00
10 g l^{-1} sucrose	4.28	3.36
10 g l^{-1} ascorbic acid	7.19	9.87

The bulk amorphous carbon samples of ascorbic acid, glucose and sucrose were prepared by heating for 2 h at 1170 K using a muffle furnace after releasing smoke. A BET specific surface area of 698 ± 17, 683 ± 17 and 624 ± 15 m^2 g^{-1} ($n = 3$) was observed for the amorphous carbon of ascorbic acid, glucose and sucrose, respectively. The pore size distribution at diameters over the range 2–20 nm (*mesopores*) is shown in Fig. 2. The adsorption average pore diameter was 2.4, 2.5 and 2.4 nm for ascorbic acid, glucose and sucrose, respectively.

Table 3 shows the effect of organic chemical modifier additive on the integrated absorbance for indium and gallium, which are elements that exhibit a large loss of analyte in GFAAS particularly when using a PG furnace because of formation of volatile oxide at 1000 K,[10,17] with a pyrolysis temperature of 900 K. The degree of sensitivity enhancement was greater for ascorbic acid than for sucrose. Although the sensitivity enhancement is due to the reduction by the pyrolysis products and the absorption onto the amorphous carbon,[9] the surface area and pore-size distribution are similar. Thus, the superiority of ascorbic acid can be elucidated by the greater yield of pyrolysis product. It has been reported in our previous work that when a PG furnace treated by a modifier at temperatures above 1230 K is used for GFAAS of indium, the superior effectiveness of ascorbic acid is also observed (Fig. 4 in ref. 9).

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