Effect of Ascorbic Acid on the Desorption of Gold in Graphite Furnace Atomic Absorption Spectrometry

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In the graphite furnace atomic absorption spectrometry of gold, signals with a single peak were observed with a pyrolytic graphite (PG) furnace, while signals with a shoulder on the tailing edge were observed with a nonpyrolytic graphite (NPG) furnace. A thermal shift of the atomic absorption signals for gold occurs in response to changes in the concentration of ascorbic acid without any loss for each furnace. When the pre-pyrolysis of a 5% (m/V) ascorbic acid solution was carried out at 1270 K, although the background signal due to the release of amorphous carbon was not observed, a thermal shift of the gold signal was confirmed. At a pre-pyrolysis temperature over 1460 K, the peak absorbance was reduced by increasing the pre-pyrolysis temperature, while absorbance at the position of the signal for gold only was increased. The values of the Arrhenius activation energy for the desorption of gold were obtained to be 60±2 kcal mol^{-1} for gold only, 93±3 kcal mol^{-1} for gold with 5% (m/V) ascorbic acid and 99±2 kcal mol^{-1} after a pre-pyrolysis of ascorbic acid at 1270 K.

Although gold is one of the most inactive metal elements, it has been reported that it interacts weakly with graphite.[1,2] It has been proposed by McNally and Holcombe[1] as well as Lynch et al.[2] that the deposition of gold as an aqueous solution leads to the formation of micro-droplets, or caps, of gold (primary site), while deposition as its vapor leads to a secondary dimensional island (secondary site) on a graphite surface. Thus, gold desorption may occur from a droplet surface or from a metal-graphite interface.

The effect of ascorbic acid on atomic vapor formation has been discussed regarding various systems.[3,4,5,6] Schcherbakov et al.[3] have proposed that the addition of ascorbic acid results in a more uniform dispersion of analyte on the furnace surfaces prior to atomization, and in the formation of reduction-active centers which are activated in the temperature range 970—1070 K. The production of some reductive gases, such as H_2, CH_4, CO, and CO_2, by the pyrolysis of ascorbic acid was also reported.[6] Sturgeon and Berman[4] have stated that ascorbic acid is completely oxidized away below 1400 K. For nickel and copper, which atomize via sublimation of the metal, no effect of ascorbic acid on their appearance temperatures (T_{app}) was observed. They also reported for gold which also atomizes via sublimation of the metal, that the T_{app} values for analyte only and ascorbic acid added were 1160 and 1600 K, respectively. Recently, a carbon-coated phase (less porous and smooth surface) was found by using scanning electron microscopy on an NPG furnace wall after pyrolyzing ascorbic acid at a temperature over 2500 K.[5]

In the present work, it was found that when a gold standard solution is introduced onto the graphite furnace, and its signal is measured after pyrolysis of 5% (m/V) ascorbic acid at 1270 K, a thermal shift of the gold signal can be observed. The Arrhenius activation energy has also been estimated. The presence of a thermally stable carbon residue at temperatures over 1400 K and the specific interaction of gold with the carbon residue are discussed in the following sections.

Experimental

Apparatus and Procedure. A Hitachi Model Z-8000 flame and graphite furnace atomic absorption spectrometer equipped with a Zeemann-effect background corrector and an optical temperature controller system (Hitachi Model 180-0341) were used. Twenty µl of sample solutions was injected by an automatic sampler. The peak height and integrated absorbance were automatically printed out and displayed on a Hitachi Data Processor. The analytical wavelength and slit width were 242.8 and 1.3 nm, respectively. The atomic absorption spectrometer was modified in our laboratory so as to allow signals with a time constant of 20 ms and temperature profiles to be registered by using an Oki personal computer (if-800 Model 50). Output data from the optical temperature controller were acquired at 4 ms intervals by the personal computer and subsequently stored on a diskette. The output data were calibrated by using the inner-wall temperature monitored by a Chino Model IR-AH1S radiation thermometer with an emissivity of unity (wavelength, 960 nm; accuracy supplied by the manufacturer, 0.5% up to 1500 K, 1.0% 2300 K, 2.0% 3300 K). The reproducibility (n=10) of ashing and the atomizing temperature for the NPG furnace was 0.5% at 800 K and 0.3% at 1419 K. The standard atomization conditions are shown in Table 1. Each measurement was performed 5 times. A commercially available stock solution of gold (1000 mg dm^{-3} of gold by $HAuCl_4$ in 1 mol dm^{-3} HCl, Wako Pure Chemical Industry Ltd.) was diluted with water to the proper concentrations before use. Distilled and de-

Table 1. Standard Atomization Conditions

Stage	Temp[a)]	Time/sec		Inner gas flow
	°C	Ramp	Hold	ml min^{-1}
Drying	120	30	0	200
Charring	700	20	5	200
Atomizing	2500	0	2	0
Cleaning	3000	0	3	200

a) Values Programmed in atomizer unit.

Table 2. Function $g(a)$ for a Controlled Reaction

Notation[a)]	$g(a)$[b)]	Notation	$g(a)$
R_1	a	F_1	$-\ln(1-a)$
R_2	$1-(1-a)^{1/2}$	$A_{3/2}$	$[-\ln(1-a)]^{2/3}$
R_3	$1-(1-a)^{1/3}$	A_2	$[-\ln(1-a)]^{1/2}$
D_1	a^2	A_3	$[-\ln(1-a)]^{1/3}$
D_2	$(1-a)\ln(1-a)+a$	A_4	$[-\ln(1-a)]^{1/4}$
D_3	$[1-(1-a)^{1/3}]^2$		
D_4	$(1-2a/3)-(1-a)^{2/3}$		

a) Notation of Sharp et al.[8)] was used. b) The function $g(a)$ is summarized by Reich and Stivala.[9)]

ionized water were further purified by a Milli-QII system.

Kinetic Method. In the present study, a well-known method involving a process for controlling the reaction rate for the solid state reaction under linear heating conditions proposed by Coats and Redfern[7)] was used for a kinetic analysis of the desorption of gold.

$$\ln[g(a)T^{-2}] = -E_aR^{-1}T^{-1} + \ln[ARP(RH)^{-1}E_a^{-1}], \qquad (1)$$

where g(a) is a function that a depending on the process controlling the reaction rate; a is a fractional conversion; RH is the heating rate; A is a frequency factor; $P=1-2X+6X^2-24X^3+120X^4+\cdots$; $X=RT/E_a$; T, E_a, and R have their usual meanings. The functions of $g(a)$ are summarized in Table 2.[8,9)] In the atomization process, the measured absorbance (A_t) at some time (t) is directly proportional to the number of analyte atoms in the vapor ($[M](g)_t$), which is also proportional to the analyte concentration released from the condensed phase. The maximum absorbance (A_{max}) is proportional to the atomic-vapor concentration at the maximum absorbance ($[M](g)_{max}$), which is also proportional to the initial concentration of analyte. Hence, we have

$$A_t = f[M](g)_t, \qquad (2)$$

$$A_{max} = f[M](g)_{max}, \qquad (3)$$

and

$$a = [M](g)_t/[M](g)_{max} = A_t/A_{max}, \qquad (4)$$

where f is a proportionality constant. If the function g (a) is properly selected in order to investigate a particular reaction, a plot of the right-hand side of Eq. 1 vs. T^{-1} should be a straight line, from whose slope the activation energy of the reaction can be calculated.

Results and Discussion

Characteristics of Atomic Absorption Signals in PG and NPG Furnaces. The atomic absorption signals for gold measured with the PG furnace under the standard atomization conditions are shown in Fig. 1, together with the observed furnace temperature profile. Figure 2 shows the raising edge of the gold signal at the first shot and at the twentieth shot when a new PG furnace was used. The T_{app} of the twentieth shot signal was lower than that of the first shot signal. A differential signal in the figure suggests the presence of a small signal with a temperature at maximum absorbance (T_{max}) of 1460±10 K. The signal at the first shot is a signal resulting from "primary desorption".[1,2)] The small signal may correspond to a signal resulting from "secondary desorption",[1,2)] due to of the lower shift of T_{app}.

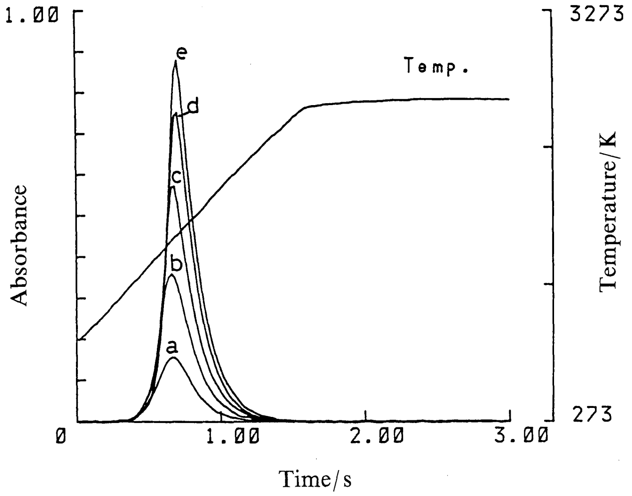

Fig. 1. Atomic absorption signals for gold with the PG furnace. Gold in µg dm^{-3}: a; 10, b; 20, c; 30, d; 40, e; 50.

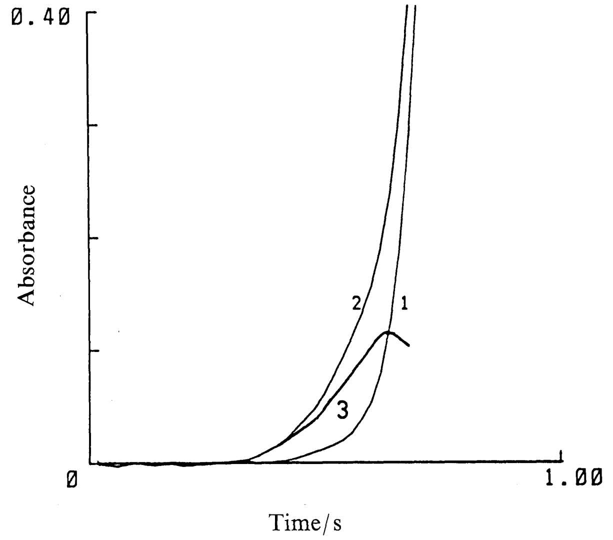

Fig. 2. Time-absorbance profile at the raising edge for gold of 50 µg dm^{-3}, when a new PG furnace was used. (1) at the first shot; (2) at the 20th shot; (3) differential profile (2)−(1).

The atomic absorption signals for gold measured with the NPG furnace under standard atomization conditions are shown in Fig. 3, together with the observed temperature profile. Signals with a shoulder on the tailing edge were observed. The formation of the shoulder can not be explained by the presence of a different atomization process due to different reduction active sites. Because no effect was found due to the addition of oxygen into the inner Ar gas on the T_{app} value of gold and it was found that gold atomizes from the metal.[1,4)] The wall of the NPG furnace is porous

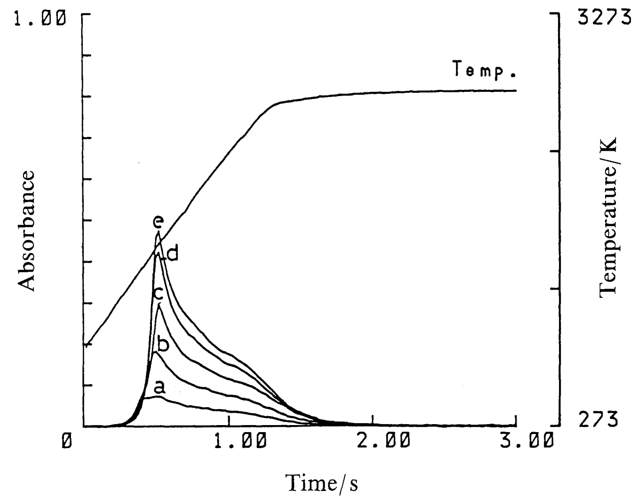

Fig. 3. Atomic absorption signals for gold with the NPG furnace. Gold in μg dm^{-3}: a; 10, b; 20, c; 30, d; 40, e; 50.

and notched, while that of the PG furnace is less porous and smooth. It is thus expected that a remarkable adsorption of gold in the furnace wall results in the appearance of the shoulder, i.e. the higher shift of formation temperature of gold atoms.

The $T_{\rm app}$ and $T_{\rm max}$ values were 1210±10 and 1570±20 K in the NPG furnace and 1220±10 and 1600±20 K in the PG furnace, respectively. The $T_{\rm app}$ and $T_{\rm max}$ values in the NPG furnace are in agreement with those in the PG furnace within the experimental error. The obtained sensitivities estimated from the peak and integrated absorbances (weight required to give 1% absorption) were 8.6 pg and 20 pg for the NPG furnace and 4.8 pg and 20 pg for the PG furnace, respectively. The sensitivities from the integrated absorbance were in agreement with each other, while the sensitivity from the peak absorbance in the NPG furnace was 1.8-times larger than that in the PG furnace. These results regarding the sensitivity can be explained by the difference in the signal shape.

Effect of Ascorbic Acid in PG and NPG Furnaces. The atomic absorptions for gold at various ascorbic acid concentrations were measured with the PG and NPG furnaces under the standard atomization conditions; thermal shifts of the gold signals occurred with changes in the concentration of ascorbic acid. Figure 4 shows their $T_{\rm app}$, $T_{\rm max}$, and integrated absorbance values. The $T_{\rm app}$ and $T_{\rm max}$ values increased with increasing the concentration of ascorbic acid without any loss in the integrated absorbance. Since the slope of the plots of $T_{\rm max}$ for the NPG furnace is greater than that for the PG furnace, the influence of ascorbic acid on the atomization of gold is emphasized in the case of the NPG furnace, rather than the PG furnace. The above results suggest that the desorption of gold was mainly due to the species adsorbed on a specific surface produced by the pyrolysis of ascorbic acid.

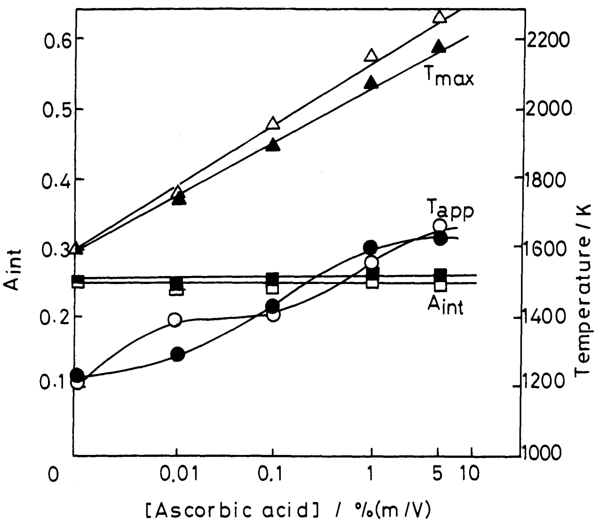

Fig. 4. Effect of the ascorbic acid concentration on the appearance temperature ($T_{\rm app}$), the temperature at maximum absorption ($T_{\rm max}$) and the integrated absorbance ($A_{\rm int}$) when the PG and NPG furnaces were used. Gold: 50 μg dm^{-3}. PG furnace: $T_{\rm app}$; ●, $T_{\rm max}$; ▲, $A_{\rm int}$; ■. NPG furnace: $T_{\rm app}$; ○, $T_{\rm max}$; △, $A_{\rm int}$; □.

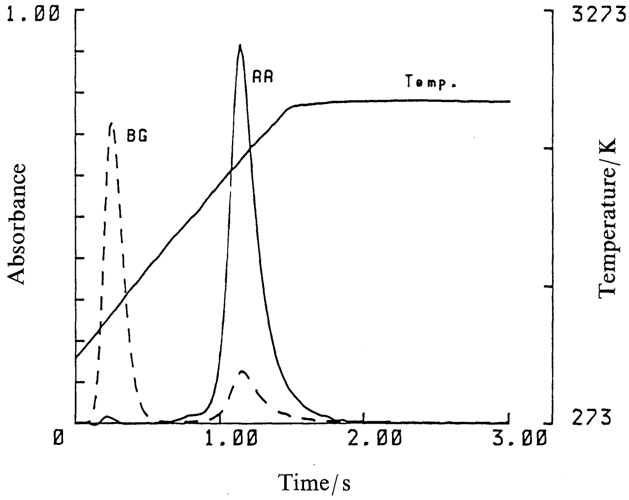

Fig. 5. Background absorption signal for 50 μg dm^{-3} of gold with 5% (m/V) ascorbic acid at 242.8 nm. BG; background absorption, AA; atomic absorption.

Effect of Pyrolyzed Ascorbic Acid. The thermal destruction of ascorbic acid forms both carbon and carbon-containing products. The formation of active centers is most pronounced in the temperature range 950—1070 K.[3] In the present work, the PG furnace was chosen to investigate the effect of pyrolyzed ascorbic acid on gold signals because of the smaller amount of adsorption of gold in the PG furnace wall. Background absorption due to ascorbic acid was observed in the range 970—1070 K before the gold signal, as shown in Fig. 5. This indicates that most of the amorphous carbon produced by pyrolysis of ascorbic acid would probably be released

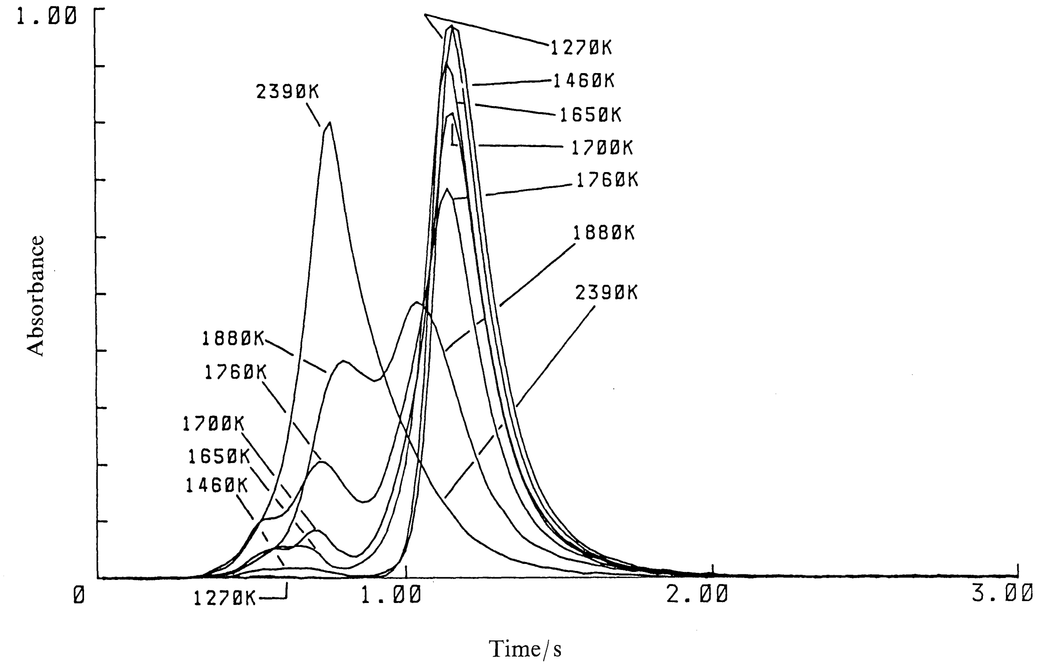

Fig. 6. Effect of pyrolyzed ascorbic acid on the atomic absorption signals of 50 μg dm^{-3} of gold. Charring temperature for pre-pyrolysis of ascorbic acid in K: 1270, 1460, 1650, 1700, 1760, 1880, 2390.

from the furnace wall within the temperature range.

In order to examine whether any pyrolysis residue of ascorbic acid exists after the appearance of the background signal, a gold standard solution (gold only) was introduced after the pyrolysis of a 5% (m/V) ascorbic acid solution; its atomic absorption was measured, where the pyrolysis of ascorbic acid is defined as pre-pyrolysis. The standard drying and charring stages were used, while the atomizing and cleaning stages were omitted in the pre-pyrolysis.

The atomic absorption signals of gold were measured over the pre-pyrolysis temperature region 670—2640 K; typical signals are shown in Fig. 6. When pre-pyrolysis was carried out at 670 K, a background signal was observed. At a pre-pyrolysis temperature of 1270 K, no background signal was observed, while a clear single peak of gold with a T_{max} of 2170±10 K was observed. This T_{max} was shifted by 570 K higher than the T_{max} of 1600±20 K obtained without ascorbic acid and was in agreement with the T_{max} of 2170±20 K obtained with 5% (m/V) ascorbic acid. At a pre-pyrolysis temperature of 1460 K, a small peak appeared at the position of the peak for gold only. At a pre-pyrolysis temperature of 1760 K, three peaks were clearly confirmed, where each peak of the triplet is defined here as the first, second, and third peaks from the low-temperature side. The absorbances at the positions of the first and second peaks were increased, and that at the position of the third peak was reduced with increasing the pre-pyrolysis temperature. The T_{max} of the first peak was 1420±10 K. This T_{max} corresponds to the T_{max} of the small signal on the

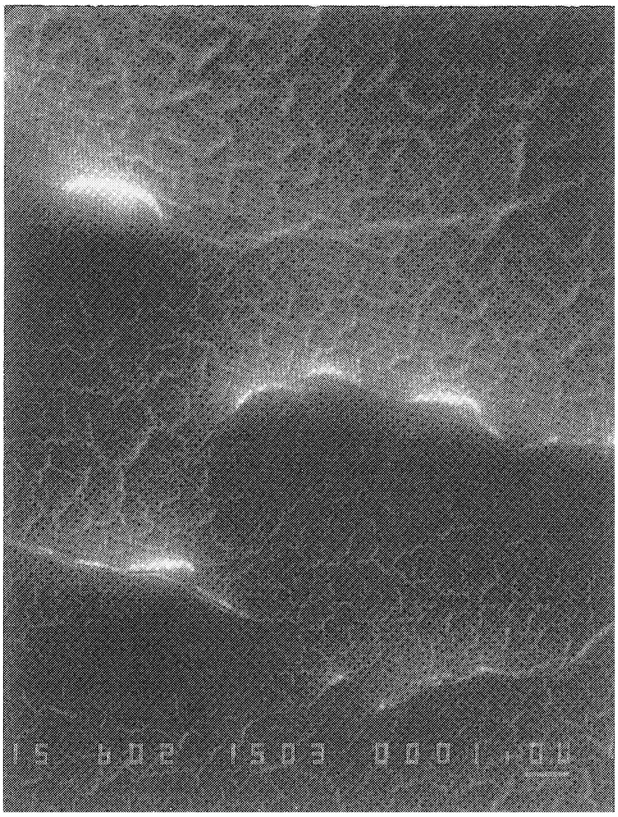

Fig. 7. Micrograph of the pyrolysis residue of ascorbic acid on the NPG furnace surface by scanning electron micrograph with 6000 magnification.

raising edge of the signal for gold only with the PG furnace (Fig. 2). The T_{max} of the second peak was 1640±20 K. This T_{max} corresponds to the T_{max} of the signal for gold only with the PG furnace. When pre-pyrolysis was carried out at 2390 K, the third peak could not be observed. The above results indicate that the pyrolysis of ascorbic acid produces some carbon residue which is stable at a temperature of the pre-pyrolysis below 1270 K, begins to be released at 1460 K, and evaporates at a temperature over 2390 K.

The formation of a thermally stable carbon residue was confirmed by scanning electron micrography (6000 magnification) of the inner furnace wall after 100 atomization cycles with 1% (m/V) ascorbic acid. A photograph is shown in Fig. 7. As can be seen in this photograph, the surface of the carbon residue is smooth with many cracks.

Kinetic Investigation. For the desorption of gold only with the PG furnace, the D_4 mechanism based on three-dimensional diffusion with spherical symmetry (Ginstling–Brounshtein equation) was chosen in order to give the best possible fits; the E_a value was obtained to be 60±2 kcal mol^{-1}. For gold in 5% (m/V) ascorbic acid, the D_4 mechanism was also chosen and the E_a value was obtained to be 99±2 kcal mol^{-1}. When a pre-pyrolysis of 5% (m/V) ascorbic acid was carried out at 1270 K, the F_1 mechanism based on the first order reaction was chosen; the E_a value was obtained to be 93±3 kcal mol^{-1}. No significant difference in the E_a value between non-pyrolyzed and pyrolyzed ascorbic acid indicates that the atomization mechanism is the same. The adsorption energy of gold on pyrolyzed ascorbic acid may be reflected in the difference in the E_a value between the presence and absence of ascorbic acid.

Since the penetration of the test solution in the furnace wall occurs for the NPG furnace, while it is negligible for the PG furnace, it is expected that as 5% (m/V) ascorbic acid was introduced, a more thermal stable carbon residue remained in the NPG furnace than the PG furnace. The influence of the characteristics of the furnace wall on the E_a value was examined. Gold in 5% (m/V) ascorbic acid was measured with the NPG furnace. The D_4 mechanism was chosen and the E_a value was obtained to be 111±2 kcal mol^{-1}. Although the best possible fitted function agrees with that in the PG furnace, the E_a value is about 10 kcal mol^{-1} larger than that in the PG furnace. This increase in the E_a value may also result from the penetration of analyte solution in the porous wall of the NPG furnace. A similar influence was observed in the thermal shift of T_{max}. However, its detailed mechanism is not known at present.

Conclusion

The pyrolysis of ascorbic acid in argon flow provides two types of pyrolyzed residue. One is amorphous carbon which is completely released away below 1100 K; the other is a thermally stable carbon residue. According to the present experimental results, it has been elucidated that gold may interact more strongly with the thermally stable carbon residue than does the PG furnace wall, resulting in a thermal shift of the gold signal.

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