KINETICS OF INDIUM ATOMIZATION FROM DIFFERENT ATOMIZER SURFACES IN ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY (ETAAS)

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Summary—The kinetic parameters of indium atomization in electrothermal atomic absorption spectrometry (ETAAS) have been determined by a newly proposed method. Effect of the atomizer surface and the palladium modifier on the kinetics of indium atomization has been investigated. The mechanisms of indium atomization seem to be identical for the pyrolytically coated graphite and the uncoated graphite tubes, *i.e.* the rate-limiting step for the atomization changes from a first order kinetics at lower temperatures into a nearly 1/3 order kinetics at higher temperatures, which may suggest that the analyte moves from a dispersed state to agglomerates with increasing temperature. However, for the zirconium coated graphite tube, the atomization of indium is controlled by a single mechanism with the kinetic order of near 2/3 and the activation energy of 186 ± 13 kJ/mol. Relatively weak indium–zirconium carbide interactions and the release of indium from the sphere of molten indium metal on the zirconium coated surface are suggested. In the presence of palladium, a simple mechanism, *i.e.* the release of indium from the solid solution of the In and the Pd on the pyrolytically coated graphite surface, is proposed to account for the observed first order kinetics and the activation energy of 421 ± 27 kJ/mol.

The atomization of analytes in electrothermal atomic absorption spectrometry (ETAAS) has been studied by many researchers based on kinetic,^{1–5} thermodynamic^{6–10} and combined kinetic–thermodynamic considerations.^{11–15} Usually, most of these reports focused on the atomization mechanisms of analytes without matrices nor modifiers from one type of graphite surface. However, it is more important to elucidate the mechanisms of analyte released in the presence of matrices or modifiers from different atomizer surfaces since normal analysis is often carried out under such conditions. Thus far, there have been a few papers appearing to deal with the atomization mechanisms of the analyte from various atomizer surfaces. Aggett and Sprott¹⁶ compared the appearance temperatures for the atomization of various analytes

from both graphite and tantalum surfaces, and concluded that the most possible mechanism for the analyte atomization from a tantalum surface was the thermal decomposition of the oxide. Gregoire *et al.*¹⁷ studied the atomization mechanisms of U, V, Mo, Ni, Mn, Cu and Mg from pyrolytic graphite and tantalum surfaces. The atomization mechanisms of various analytes from molybdenum¹⁸ and tungsten¹⁹ surfaces were compared with those from the graphite surface. Gao and Ni²⁰ suggested that the atomization mechanism of germanium in the zirconium coated graphite tube was the vaporization of germanium following the reduction of GeO₂ or GeO by zirconium carbide, which was different from the thermal decomposition mechanism of the oxide in the uncoated graphite tube. Recently, Chakrabarti and Cathum²¹ investigated the mechanism of cobalt atomization from different atomizer surfaces in ETAAS, and suggested that the atomization mechanism of

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cobalt seemed to be the same for the pyrolytically coated graphite and the uncoated electrographite surfaces, but different for the glassy carbon furnace. Fonseca *et al.*²² studied the vaporization/atomization characteristics of Cu sample from graphite and Ta-lined tubes using both Ta and graphite platforms and found first order release of Cu from both Ta and graphite surfaces.

Much less attention has been paid to the behavior of indium in the graphite furnace compared with other analytes. Grinshtein *et al.*²³ studied the interaction between indium and the graphite surface at various temperatures by using a tube-in-tube, spatially isothermal furnace. At temperatures less than 1900 K, indium adsorbed to the graphite surface and the effective residence time of this element was greater than theoretically predicted residence time. However, at temperatures greater than 1900 K, no significant adsorption of In occurred. In an earlier study, Katskov *et al.*²⁴ determined an activation energy of 234 kJ/mol at lower temperatures followed by 134 kJ/mol at higher temperatures for the atomization of In. Recently, McNally and Holcombe²⁵ studied the topology and vaporization characteristics of indium in a CRA- 90 min. Massmann furnace. Two activation energies of 238 ± 29 and 138 ± 21 kJ/mol were obtained over the course of release from In using manual pipetting. An appearance order of greater than one was suggested for indium release from the concentration study, and the aggregate surface was proposed as one of the generation mechanisms for indium. They also observed the relatively weak interaction between indium and graphite.

The purpose of this work is to study the atomization kinetics of indium from different atomizer surfaces, *i.e.* pyrolytically coated, uncoated and zirconium coated graphite surfaces, and the effect of the palladium modifier on the kinetics of indium atomization from the pyrolytically coated graphite surface by using a newly proposed method.²⁶

THEORY

In a previous report,²⁶ a method was developed for the simultaneous determination of the kinetic parameters of atom formation from a single absorbance signal profile under normal analytical conditions in electrothermal atomic absorption spectrometry (ETAAS). The change

of the absorbance, A , with time, t , was given by the following equation:

$$dA/dt = P^{x-1}k_1 \left(\int_t^\infty k_2 A dt - A \right)^x - k_2 A \quad (1)$$

where k_1 and k_2 are the temperature and subsequently time dependent rate constants for the formation and dissipation of gaseous atoms, respectively; P a proportionality factor, x the kinetic order of the atom formation reaction. According to the Arrhenius' law, the temperature dependence of k_1 can be expressed as follows:

$$k_1 = k_0 \cdot \exp(-E_a/RT) \quad (2)$$

where k_0 and E_a are the frequency factor and activation energy for atom formation, respectively; R the gas constant and T the absolute temperature at time t . Substituting equation (2) into equation (1) and rearranging yields:

$$dA/dt + k_2 A = k_0 P^{x-1} \times \left(\int_t^\infty k_2 A dt - A \right)^x \cdot \exp(-E_a/RT) \quad (3)$$

Taking logarithm of equation (3), differentiating and rearranging give

$$\Delta \ln(dA/dt + k_2 A) / \Delta \ln \left(\int_t^\infty k_2 A dt - A \right) = x - (E_a/R) \Delta(1/T) / \Delta \ln \left(\int_t^\infty k_2 A dt - A \right). \quad (4)$$

Equation (4) shows that if the atomization of the analyte from the atomizer surface is governed by a single kinetic mechanism, a plot of $\Delta \ln(dA/dt + k_2 A) / \Delta \ln(\int_t^\infty k_2 A dt - A)$ vs $\Delta(1/T) / \Delta \ln(\int_t^\infty k_2 A dt - A)$ should be a straight line. From the slope of such a plot, the activation energy (E_a) can be calculated, while the kinetic order (x) can be obtained from the intercept. The validity of equation (4) has been confirmed both by computer simulation study^{26,27} and the ETAAS experiments.²⁶

To obtain the kinetic order and activation energy by using equation (4), the temperature dependence of k_2 should be known. In this study, the gas-stop mode is used in the atomization step and the dissipation of the analyte by convection is distinctly negligible. Therefore, k_2 is the total rate constant for the dissipation of the analyte by diffusion and thermal expansion only, *i.e.*

$$k_2 = k_d + k_e \quad (5)$$

where k_d and k_e are the constants for atom dissipation by diffusion and thermal expansion at any time, respectively; K_d is defined as²⁸

$$k_d = k_d^0 (T/T_0)^y \quad (6)$$

where k_a and k_d^0 are diffusional rate constants at temperature T and T_0 , respectively; y varies between 1.5 and 2.0,²⁸ K_e is given by²⁹

$$k_e = (dT/dt)/T \quad (7)$$

where dT/dt is the heating rate at any temperature T .

For determining the temperature dependence of k_2 , the values of k_d^0 and y should be obtained. For indium, the y value of 1.84 can be found from Ref. 30. The value of k_d^0 can be determined from the decay portion of the absorbance signal profile based on the method proposed by Akman *et al.*²⁹

To determine E_a and x based on equation (4), the terms of dA/dt and $\int_i^\infty k_2 A dt$ should be calculated. To this end, mathematical expressions of $A = f_1(t)$ and $k_2 A = f_2(t)$ are obtained by polynomial regressions. Thus, the functions of $dA/dt = f'_1(t)$ and $\int_i^\infty k_2 A dt = F_2(t)$ can be obtained by differentiating the expression of $A = f_1(t)$, and integrating $k_2 A = f_2(t)$, respectively.

Data from the appearance to the maximum in the absorbance signal can be used to construct the plot based on equation (4) for determination of the kinetic order and activation energy since the amount of the analyte unatomized on the tube surface at time t , $P(\int_i^\infty k_2 A dt - A)$, is greater than zero from the beginning at least to the maximum in the signal. In addition, special conditions to isolate the supply and removal function, and linear temperature ramp are indeed not required with the use of equation (4) because of no such assumptions made during the derivation of equation (4).

EXPERIMENTAL

Apparatus

A Perkin-Elmer model 4000 atomic absorption spectrometer, equipped with a deuterium background corrector and a model HGA-400 graphite furnace was used for the measurement of the atomic absorption in the gas-stop mode. An indium hollow-cathode lamp (Shanghai Tienkuang Scientific Instruments Works, Shanghai, China) was employed at a lamp current of 5 mA. The 303.9 nm line of indium was

Table 1. Furnace programme

	Dry	Ash	Atomize	Clean
Ramp time (sec)	20	5	1	1
Hold time (sec)	50	30	5	2
Temperature (°C)	130	Various	Various	2650
Int. gas flow (ml/min)	300	300	0	300

used as the analysis line, with a spectral band-pass of 0.7 nm. High purity argon gas was used as both sheath and purge gas. The furnace programme is given in Table 1.

The graphite tube wall temperature was obtained from the output of a germanium phototransistor (B 1918-01, Hamamatsu), which was calibrated by focusing a disappearing filament optical pyrometer (Ircon Inc., UX-10, USA) through the sample injection hole in the graphite tube. The absorbance and temperature signal were synchronously acquired by a microcomputer-based data acquisition system at 20-msec intervals.²⁶ The signals could be subsequently stored on a diskette for further use.

Three different atomizer surfaces were used for the atomization of indium: Pyrolytically coated (PG), uncoated graphite tubes (UG) and the zirconium coated PG (ZrPG). The ZrPG were prepared according to Ref. 31.

Reagents

The stock solution containing 1000 mg/ml In was prepared by dissolving In_2O_3 in an adequate volume of diluted nitric acid and subsequently diluting with deionized water. Working standards of the element were prepared daily from this stock solution with deionized water just before use. Indium working solutions were manually introduced into the furnace in 20- μl volumes using an Eppendorf pipette.

A 5% m/v of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ solution was prepared by dissolving $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in diluted nitric acid and then diluting with deionized water.

All chemicals were of analytical-reagent grade.

RESULTS AND DISCUSSION

Atomization from the pyrolytically coated graphite tube (PG)

The concentration study, which is illustrated in Fig. 1, contains absorbance-time plots for various initial masses of In deposited on the

Fig. 1. Absorbance signal profiles for various masses of In from the pyrolytically coated graphite tube: (a) 5 (b) 3 (c) 2 (d) 1 (e) 0.5 ng. Ashing temperature: 500°C, atomization temperature: 2600°C, other conditions as listed in Table 1.

bottom of the PG. As the initial amount of In deposited on the surface of the PG is increased, peak times are similar and there is a slight shift to earlier appearance times. Thus, the apparent kinetic order for indium atomization from the PG appears to be unity.²⁵ To obtain the kinetic order of indium atomization accurately, the plot of $\Delta \ln(dA/dt + k_2 A) / \Delta \ln(\int_0^\infty k_2 A dt - A)$ vs $\Delta(1/T) / \Delta \ln(\int_0^\infty k_2 A dt - A)$ is constructed from the absorbance signal profile. Figure 2 shows such a plot obtained from Fig. 1(c). As can be seen, the plot exhibits curvature, and so assignment of a single straight line from this plot is difficult, which may, in fact, reflect a continuous varying slope. This could imply gas-phase dissociation as step governing atom formation or a temperature dependence of activation energy (E_a) and kinetic order (x) on surface coverage. Figure 3 shows the decomposition (curve A) and atomization (curve B) curves for indium from the PG. As can be seen, there is a gap between the temperature in the decomposition curve at which the absorbance begins to decrease (the maximum tolerant ashing temperature), and the appearance temperature in the atomization

Fig. 2. Plot obtained from Fig. 1(c) based on equation (4) for 2 ng of In from the pyrolytically coated graphite tube.

Fig. 3. Decomposition and atomization curves for 0.5 ng of In by atomization from the pyrolytically coated graphite tube; (a) decomposition curve, at the atomization temperature of 2600°C (b) atomization curve, at the ashing temperature of 500°C, and from the zirconium coated graphite tube; (c) decomposition curve, at the atomization temperature of 2400°C and (d) atomization curve, at the ashing temperature of 800°C.

curve. This means that the decrease in the absorbance is not only due to loss of $\text{In}_{(g)}$ but also to the formation of other gaseous species at temperatures above 700°C. Calculations of thermodynamic equilibrium in the In–O–C system over the temperature range of 500–2000 K have shown that $\text{In}_2\text{O}_{(g)}$ is likely to be formed at either high ashing or lower atomization temperatures, but that $\text{InO}_{(g)}$ should not play a significant role in the atomization of In.³² This has been confirmed by means of graphite furnace-mass spectrometry (GFMS) experiment.³² However, it is not easy to discuss the formation of free indium via gas-phase dissociation of an oxide in terms of kinetics since one must take into account the change in partial pressure of oxygen as well as the generation function of the indium oxide from the surface and the generation of the metal from the gas.³³

An alternative explanation for the curvature observed in Fig. 2 may be that multiple release mechanisms contribute to the atomization of indium from the PG surface. If two straight lines are used to fit the plot in Fig. 2, then the activation energy (E_a) and kinetic order (x) could be found to be 134 kJ/mol and 0.97 at lower temperatures, 63 kJ/mol and 0.37 at higher temperatures, respectively. This probably indicates that the rate-limiting step for the atomization of indium changes from a nearly first order kinetics with larger E_a value at lower temperatures into the kinetics of $x = 0.37$ with lower E_a value at higher temperatures.

If we assume that either two straight lines or a continuous curve exists in Fig. 2 and that the

intercept of any portion of the curve (*i.e.* the kinetic order x) would represent the state of the morphology of the analyte on the surface at that time, then one could conclude that the material moves from a dispersed state of $x = 1$ to agglomerates (*i.e.* $x = 0.37$). This suggests that the analyte begins as dispersed atoms or molecules containing indium and then forms droplets with increasing temperature. Although indium metal indeed exhibits weak interactions at the graphite observed by McNally and Holcombe,²⁵ some indium molecular species may have a strong interaction which causes it to be dispersed on the surface and exhibited nearly first order release at lower temperatures. The obtained larger E_a value (134 kJ/mol) could represent indium molecular species-graphite interaction energy. Furthermore, the weak indium metal-graphite interactions would foster the formation of droplets which is consistent with the higher temperature order of release ($x = 0.37$). The observed lower E_a value may represent the energy required for indium release at the edge of the metal-graphite interface.^{25,34} It is possible that indium metal would be formed either through carbon reduction of the oxide or the thermal decomposition of the oxide at higher temperatures. In addition, no significant influence of the initial injected mass of indium studied on the indium atomization from the PG is observed, as shown in Table 2.

Fig. 4. Plot constructed based on equation (4) for 2 ng of In from the uncoated graphite tube. Other conditions as in Table 1.

Atomization from the uncoated graphite tube (UG)

In order to examine surface spreading and penetration by the aqueous solution of the sample on the atomization of indium, the kinetic parameters of indium atomization from the uncoated graphite tube (UG) have been determined. Figure 4 illustrates the plot of $\Delta \ln(dA/dt + k_2A)/\Delta \ln(\int_0^\infty k_2A dt - A)$ vs $\Delta(1/T)/\Delta \ln(\int_0^\infty k_2A dt - A)$ from the absorbance signal profile for 2 ng of indium ashed at 500°C and atomized at 2600°C from the UG. Compared with Fig. 2, similar results can be obtained from Fig. 4, *i.e.* Fig. 4 also exhibits nonlinearity, reflecting a continuous varying slope and intercept. If two straight lines are

Table 2. Kinetic parameters for indium atomization from different atomizer surfaces ($\pm$ standard deviation of three determinations)

Tube	Mass of In (ng)	Kinetic order	E_a (kJ/mol)
PG	0.5	$0.35 \pm 0.05/0.97 \pm 0.05$	$50 \pm 13/138 \pm 13$
	1	$0.36 \pm 0.03/0.96 \pm 0.03$	$51 \pm 12/142 \pm 13$
	2	$0.40 \pm 0.04/0.99 \pm 0.06$	$63 \pm 10/146 \pm 13$
	3	$0.37 \pm 0.01/0.98 \pm 0.07$	$50 \pm 4 /138 \pm 15$
	5	$0.37 \pm 0.04/1.02 \pm 0.06$	$42 \pm 4 /126 \pm 17$
	Av.	$0.37 \pm 0.02/0.98 \pm 0.02$	$51 \pm 7 /138 \pm 8$
UG	0.5	$0.38 \pm 0.02/0.95 \pm 0.06$	$56 \pm 8 /142 \pm 17$
	1	$0.34 \pm 0.04/0.98 \pm 0.04$	$50 \pm 10/126 \pm 13$
	2	$0.36 \pm 0.06/0.94 \pm 0.07$	$54 \pm 15/138 \pm 17$
	3	$0.37 \pm 0.02/1.04 \pm 0.05$	$50 \pm 6 /134 \pm 13$
	5	$0.35 \pm 0.04/1.02 \pm 0.06$	$59 \pm 13/126 \pm 8$
	Av.	$0.36 \pm 0.02/0.98 \pm 0.04$	$54 \pm 4 /133 \pm 8$
PG + Pd	0.25	1.04 ± 0.06	406 ± 25
	0.5	1.02 ± 0.07	460 ± 25
	0.75	1.08 ± 0.11	414 ± 8
	1	1.08 ± 0.09	402 ± 20
	Av.	1.06 ± 0.03	421 ± 27
ZrPG	0.25	0.61 ± 0.07	204 ± 6
	0.5	0.69 ± 0.05	185 ± 11
	0.7	0.59 ± 0.04	174 ± 10
	0.9	0.68 ± 0.09	180 ± 13
	Av.	0.64 ± 0.05	186 ± 13

used to fit Fig. 4, the kinetic order and activation energy can be found to be 0.97 and 155 kJ/mol, at lower temperatures, respectively; while at higher temperatures, the kinetic order of 0.38 and activation energy of 67 kJ/mol can be obtained. Although the uncoated graphite surface is expected to show much more porous than the pyrolytically coated graphite surface, the near identity of the kinetic parameters indicates that the atomization mechanisms of indium are similar for both atomizer surfaces.

Atomization from the PG surface in the presence of palladium

It has been shown that palladium is an effective matrix modifier for the determination of indium, which greatly improves the sensitivity and raises the maximum tolerant ashing temperature.³⁵ In this work, the effect of the presence of palladium on the atomization mechanism of indium is investigated. The palladium modifier is pretreated before each determination by injecting a 20 μ l of 100 μ g/ml Pd into the PG through the sample injection hole, drying at 150°C for 30 s and heating at 900°C for 30 sec. Figure 5 shows the plot of $\Delta \ln(dA/dt + k_2 A) / \Delta \ln(\int_0^\infty k_2 A dt - A)$ vs $\Delta(1/T) / \Delta \ln(\int_0^\infty k_2 A dt - A)$ from the absorbance signal profile for 0.5 ng of In ashed at 500°C and atomized at 2600°C from the PG surface in the presence of palladium. In contrast to Figs 2 and 4, a single straight line can be fit well to the plot shown in Fig. 5. This means that a single mechanism is active in the atomization of indium with palladium. From Fig. 5 the activation energy and kinetic order are found to be 414 kJ/mol and 0.95, respectively. No significant influence of the initial injected mass of indium studied on the kinetics of indium atomization is observed, as shown in

Fig. 5. Plot obtained by using equation (4) for 0.5 ng of In in the presence of 2 μ g of Pd from the pyrolytically coated graphite tube. Other conditions as in Fig. 1.

Fig. 6. Absorbance signal profiles for various masses of In from the pyrolytically coated graphite tube when 2 μ g of Pd is used as a modifier: (a) 1; (b) 0.75; (c) 0.5; (d) 0.25 ng. Other conditions as in Fig. 1.

Table 2. The first order kinetics can also be seen from the concentration study depicted in Fig. 6. These results suggest that the atomization mechanism of indium in the presence of palladium is different from those for the PG and UG in the absence of palladium.

Figure 7 shows the absorbance signal profiles for 0.5 ng of In ashed at 500°C and atomized at 2600°C from the PG with (curve A) and without (curve B) the palladium modifier. Obviously, in the presence of palladium the appearance of the absorbance signal is significantly delayed, and both the peak height and peak area are increased. The increase in the sensitivity indicates that the use of a palladium modifier prevents the formation of gaseous species in the presence of palladium. By using Fourier transform infrared spectrometry, Volynsky *et al.*³⁶ found that the palladium modifier sharply decreased the reduction temperature of the metal oxides with graphite. It was regarded that the catalytic property of palladium facilitated the carbon reduction of oxides at low ashing temperatures.³⁶ Thus, we assume that in the presence of palladium the oxide $\text{In}_2\text{O}_{3(s)}$ is rapidly reduced to metallic indium, and the resultant indium metal forms the intermetallic compounds or solid solution^{37,38} with the

Fig. 7. Effect of palladium modifier on the absorbance signal profile of indium from the pyrolytically coated graphite tube: (a) 0.5 ng In + 2 μ g Pd; (b) 0.5 ng In. Conditions as shown in Fig. 1.

palladium metal, thus decreasing or almost eliminating loss of the analyte due to the formation of gaseous oxide. At the atomization stage, the absorbance is produced owing to the release of indium from the solid solution with Pd, which may cause the observed first order kinetics. The obtained E_a value (421 ± 27 kJ/mol) represents the energy required to release the indium in molten palladium, which depends on the heat of solution of the In and the pd.

Atomization from the zirconium coated graphite tube (ZrPG)

The absorbance signal profiles for different amounts of indium atomized from the zirconium coated graphite tube (ZrPG) under optimum conditions are depicted in Fig. 8, from which the fractional kinetic order for the atomization of indium from the ZrPG can be seen since the peak maximum occurs later with increasing analyte mass.³⁴ In order to obtain the accurate value of the kinetic order, plots of $\Delta \ln(dA/dt + k_2 A) / \Delta \ln(\int_0^\infty k_2 A dt - A)$ vs $\Delta(1/T) / \Delta \ln(\int_0^\infty k_2 A dt - A)$ are constructed. Figure 9 shows such a plot from Fig. 8(d). The obtained values of the kinetic order and activation energy from Fig. 9 are 0.64 and 192 kJ/mol, respectively. There is no remarkable change in the kinetic parameters for indium atomization from the ZrPG with the initial injected amount of In studied, as can be seen from Table 2. The above results imply that the atomization mechanisms of indium are different for the ZrPG and PG.

Figure 3 also shows the decomposition (curve C) and atomization (curve D) curves for indium from the ZrPG. As can be seen, there is no significant gap between the maximum tolerant ashing temperature and the appearance

Fig. 8. Absorbance signals for various amounts of In from the zirconium coated graphite tube: (a) 0.9 (b) 0.7 (c) 0.5 (d) 0.25 ng. Ashing temperature: 800°C, atomization temperature: 2400°C.

Fig. 9. Plot obtained from Fig. 8(d) by using equation (4) for 0.25 ng of In from the zirconium coated graphite tube.

temperature in the atomization curve. Thus, compared with the PG (curves A and B in Fig. 3), the ZrPG seems to prevent the formation of gaseous species and greatly improves the sensitivity. It has been suggested that prevention of oxide formation may be the main reason for the better sensitivity of determinations on the refractory element coated furnace.³⁹ Probably more active reducing properties of refractory element carbides than graphite are responsible for the prevention of gaseous oxide formation.^{20,40} Increase in the absorbance with ashing temperature below 700°C (curve C in Fig. 3) indicates that the reducing activity of ZrC may increase with temperature.

On the basis of the above, the following reactions are supposed for indium atomization from the ZrPG, similar to those discussed in Refs 20, 41;

The resulting metallic zirconium reacts with graphite to form ZrC again at high temperatures, while the formed indium metal vaporizes with increasing temperature. The obtained kinetic order of near 2/3, along with the activation energy of 192 kJ/mol, indicates that the atomization of indium may be governed by the surface area of the sphere of molten metal, and the interaction between indium metal and zirconium carbide surface is relatively weak.

CONCLUSION

The kinetics of indium atomization seems to be similar for the pyrolytically coated and the

uncoated graphite tubes, but different for the zirconium coated graphite tube. The use of a palladium modifier or of the zirconium coated tube changes the path of indium atomization, inhibiting the formation of gaseous indium oxide, and hence greatly improves the sensitivity for indium determination.

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