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Reduction of metal oxides by carbon in graphite furnaces

Part 2.† Temporal oscillations in atomic absorption during the process of slow evaporation of Al, Mn and Yb oxides in spatially isothermal and non-isothermal graphite atomizers‡

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Temporal oscillations in the kinetics of carbothermal reduction of Al, Mn and Yb oxides in spatially isothermal side-heated tubes were investigated in the first part of this study. Microgram amounts of the elements, as their nitrates, were evaporated during slow heating ($1\text{--}20\text{ K s}^{-1}$) of the graphite tube. Several features of this phenomenon were investigated, including the effects of sample mass and solution volume, the influence of Sr and the type (Ar and N₂) and flow rate ($0\text{--}250\text{ ml min}^{-1}$) of sheath gas on the character of the atomic absorption spikes. Essentially, all effects were similar to those found with spatially non-isothermal tubes. Results of possible effects of condensation/re-evaporation processes on temporal oscillations of atomic absorption signals from Al and Yb oxides in spatially non-isothermal tubes are presented in the second part of this study. No influence of transport processes on the temporal oscillations during common conditions of sampling and heating was evident. The results suggest that the origin of the temporal oscillations lies with the primary sample residue. All the above support the gaseous carbide mechanism of formation of temporal oscillations in the atomic absorption signals.

One of the most interesting features of the process of evaporation of microgram masses of metal oxides during slow heating (about 10 K s^{-1}) of the graphite tube is the temporal oscillation in the kinetics of oxide evaporation manifested in the periodic appearance of fast absorption spikes. A complete bibliography of this subject has been reported in Part 1 of this series of papers.¹ This phenomenon was interpreted by L'vov *et al.*² in the framework of the gaseous carbide theory. Owing to the oxide particles being cooled by the spike formation process, the gaseous carbides are decomposed and the carbon, thus produced, forms a film at the oxide surface. This film terminates the autocatalytic reaction responsible for spike formation and is removed by oxidation with subsequent re-initiation of the process.

An alternative attempt to explain this phenomenon is based on the redistribution of sample within the atomizer. Ohlsson *et al.*³ and Lamoureux *et al.*⁴ suggested that spike repetition was primarily associated with condensation/re-evaporation processes in connection with a large longitudinal temperature gradient within end-heated atomizers. Two principal arguments were used to support their hypotheses. The first one is based on the difference in the number of spikes observed during the evaporation of the same masses of alumina (ranging from 30 ng to 1 µg of Al) in end-heated spatially non-isothermal and side-heated spatially isothermal atomizers. In contrast to several (up to six) spikes observed by L'vov⁵ when using an end-heated tube, only one spike was observed³ for a side-heated tube. Argon was used as the purge gas in both cases.

A further argument in support of a "redistribution" origin for these temporal oscillations is based on the results of observation

of sample deposition on the cooler parts of the atomizer. Ohlsson *et al.*³ introduced an Al(NO₃)₃ solution (200 ng Al) onto the wall of a spatially isothermal tube. After drying, a platform was inserted and the heating started (10 K s^{-1}). Heating of the tube was terminated just after the first spike, whereupon the platform was removed and the tube again heated to remove any residue. The platform was then re-inserted and run through the full temperature program. A second spike was obtained from an Al compound which evidently had been transported to the platform during the first spike.

Lamoureux *et al.*⁴ used an end-heated tube in their experiments. The heating rate was 10 K s^{-1} . When the temperature of the tube reached 1800 °C, a tantalum probe with an Al microparticle (metallic state) was inserted into the furnace for 10 s and then removed. Immediately after the insertion of the probe the absorption signal went off scale because of the large amount of Al introduced into the furnace. Upon removal of the probe, the signal returned to the baseline, but was then followed by a succession of spikes, even though the initial source of Al had been removed. The authors⁴ concluded that Al spikes can be formed not only by atomization of Al from the initial source, but also by a secondary process, and that the repeated appearance of Al spikes is due to the same secondary process.

These arguments were subsequently discussed by L'vov.⁶ Based on the results of preliminary experiments with Al and Mn oxides evaporated in a spatially isothermal THGA tube, he concluded that spike repetition is a phenomenon as characteristic of spatially isothermal furnaces as it is of non-isothermal furnaces. As for the role of sample redistribution, L'vov⁵ noted that "the process of sample transport to and condensation at the cold ends is not capable of explaining the discreteness in spike repetition".

†For Part 1 see ref. 1.

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Table 1 Operating conditions for Model 4100ZL spectrometer

Element	Wavelength/nm	Slit width/nm	Heating program			
			Temperature/°C	Ramp time/s	Hold time/s	Gas flow/ml min ⁻¹
Al	309.3	0.7	110	1	30	250
			130	5	50	250
			1600	10	6	50
			2300	50	1	50
			2500	2	10	250
Mn	403.1	0.2	110	1	30	250
			130	5	50	250
			1120	10	6	250
			1170	50	1	250
			2400	10	10	250
Yb	398.8	0.7	110	1	30	250
			130	5	50	250
			1500	10	6	50
			2100	50	1	50
			2400	10	10	250

The primary purpose of this study was to investigate the role of spatial non-isothermality in such temporal oscillations more carefully. To this end, the vaporisation characteristics of Al, Mn and Yb oxides were examined in both spatially isothermal (THGA) and spatially non-isothermal (HGA) systems.

Experimental

Instrumentation and reagents

All experiments with a spatially isothermal tube were conducted with a Perkin–Elmer (Norwalk, CT, USA) Model 4100ZL spectrometer fitted with an AS-70 autosampler. The light sources comprised an LSP-2 hollow cathode lamp (HCL) for Al (made in Russia) and Perkin–Elmer Intensitron HCL's for Mn and Yb. Standard and end-capped THGA tubes were employed. Argon and nitrogen, containing not more than 10⁻³% O₂, served as sheath gases.

All experiments with a spatially non-isothermal tube were made using a Perkin–Elmer Model 5000 spectrometer equipped with an HGA-500 graphite atomizer and an AS-40 autosampler. Absorption profiles were registered using a personal computer and a laboratory developed program. Standard pyrolytic graphite coated tubes and small pieces of pyrolytic graphite platforms (4 × 5 mm²) were employed. Argon served as a sheath gas. Stock solutions were prepared from reagent grade chemicals.

Procedures

In experiments with a spatially isothermal furnace, several parameters were varied to obtain optimal conditions for the observation of temporal oscillations and the examination of the general features of this phenomenon: sampling mass (0.1–13 µg Al, 1.5–20 µg Mn and 0.1–5 µg Yb), heating rate (1–20 K s⁻¹), volume and concentration of solutions injected, type of sheath

gas (Ar or N₂), gas flow rate (0–250 ml min⁻¹) and mass of Sr (0.1–25 µg Sr) added to the sample solution in some cases. To eliminate the magnet overheating, all measurements were performed in “single beam” mode with the magnet switched off. Typical conditions for observation of temporal oscillations (without Sr addition) are presented in Table 1. Results from all optimised experiments were repeated 2–3 times.

The principal goal of experiments with non-isothermal HGA tubes was to investigate the possible effect of condensation/re-evaporation processes on the temporal oscillations of signals from Al and Yb oxides. To localise the area for the primary source of evaporation, 10 µl of analyte solution were injected through the dosing hole of the tube and deposited on a small piece of platform. After the drying (200 °C) and charring (1700 °C) steps, the tube was heated to 2300 °C. A full flow of Ar (300 ml min⁻¹) was used in all steps (see Table 2 for other experimental parameters). After obtaining more or less reproducible temporal oscillation profiles (a), the experiment was repeated but heating was interrupted just after the second spike (b). After removing the platform from the tube, the heating of the empty tube was resumed to eliminate any residual sample (c). Thereafter, the platform was introduced into the tube and the heating program again repeated (d). For comparison, experiments with the interruption in heating, but without removal of the platform, were also performed (only the second and final steps were used). All profiles for both oxides were used to reveal any transport effect on temporal oscillations.

Results and discussion

Spatially isothermal tube

Effect of graphite substrate. Although graphite substrate conditions are of primary importance to the generation of

Table 2 Operating conditions for Model 5000 spectrometer

Element	Wavelength/nm	Slit width/nm	Mass/µg	Heating program			
				Temperature/°C	Ramp time/s	Hold time/s	Ar flow/ml min ⁻¹
Al	309.3	0.2	6	200	10	50	300
				1700	1	5	300
				2300	60	0	300
Yb	267.2	0.2	4	200	10	50	300
				1700	1	5	300
				2300	70	0	300

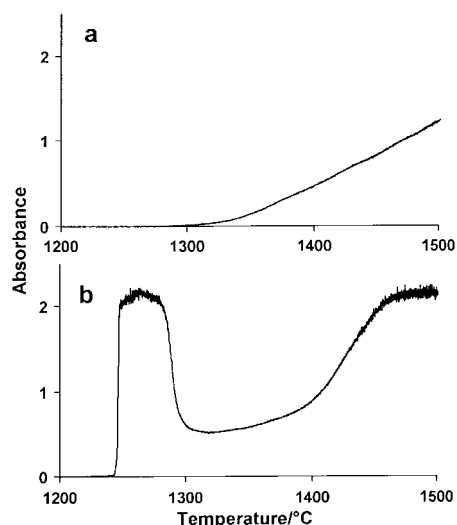


Fig. 1 Absorption profiles for 15 µg Mn evaporated at a heating rate 6 K s^{-1} from the surface of new (a) and old (b) THGA tube into an Ar atmosphere (0 ml min^{-1}).

temporal signal oscillations from Mn oxide, there is practically no effect on this phenomenon for signals from Al and Yb oxides. Fig. 1 illustrates the difference in absorption profiles for evaporation of 15 µg of Mn from the surface of new (a) and old (b) standard THGA tubes. The broad rectangular pulse at 1250°C with a very steep front and tail (heating rate was 66 K s^{-1}) originates from the process of autocatalytic reduction of oxide by carbon. The slow increase of Mn absorption at 1300°C occurs as a result of thermal dissociation of the oxide. For Al and Yb oxides, variations in graphite surface substrate (new or old tubes, platform or wall evaporation and standard or end-capped tubes) produce no significant differences in the appearance temperature and shape of the oscillation profiles.

Effect of sample mass. Fig. 2 illustrates the effect of sample mass on the absorption profile for Al in Ar. It is seen that the number of spikes and the width of the first spike increase with sample mass. For masses lower than 1 µg , only one spike was typically observed. This correlates with observations by Ohlsson *et al.*³ The width of the first spike varies nearly proportionally with the mass of Al, in agreement with our observations of this effect in a non-isothermal HGA tube.¹

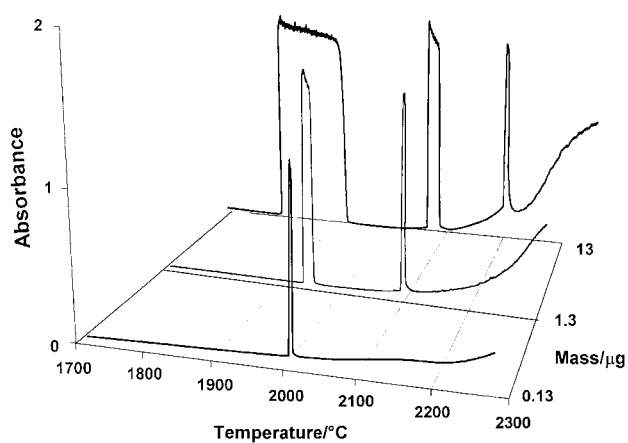


Fig. 2 Absorption profiles for Al (different masses) evaporated at a heating rate 14 K s^{-1} in a THGA tube into an Ar atmosphere (50 ml min^{-1}).

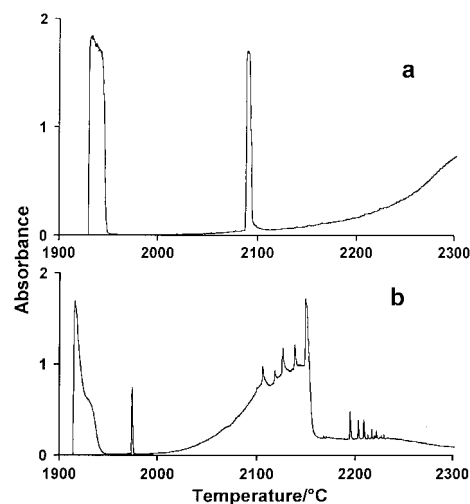


Fig. 3 Absorption profiles for 1.3 µg Al evaporated at a heating rate 14 K s^{-1} in a THGA tube into Ar (a) and N_2 (b) atmospheres (50 ml min^{-1}).

Effect of type of sheath gas. Figs. 3 and 4 illustrate the effect of sheath gas type (Ar and N_2) on temporal oscillations for Al and Yb. As can be seen, the number of spikes increases in N_2 , but their mean peak height is reduced. Manganese exhibited this same trend. In most cases, the appearance temperature in N_2 is lower than that in Ar. These observations are in agreement with those reported for non-isothermal HGA tubes.⁵ The reduction of the intervals between spikes in N_2 may be connected to an additional reaction between the carbon film formed on the oxide particles and nitrogen, *i.e.*, $2\text{C(s)} + \text{N}_2 \rightarrow 2\text{CN}$.

Effect of volume of injected solution. Fig. 5 shows the effect of solution volume injected into the tube on the absorption profile. In both cases (a and b), 2.5 µg of Al was introduced but in case (b) the volume was 10 times larger than in case (a). This resulted in a significant increase in the number of spikes. At the same time, the width of the first spike was significantly reduced. A similar effect has been observed for Yb oxide in experiments with a spatially non-isothermal HGA tube.² It is likely that this is due to the smaller particle size in case (b) and, as a result, decreased intensity of the autocatalytic process and smaller density of the carbon film.

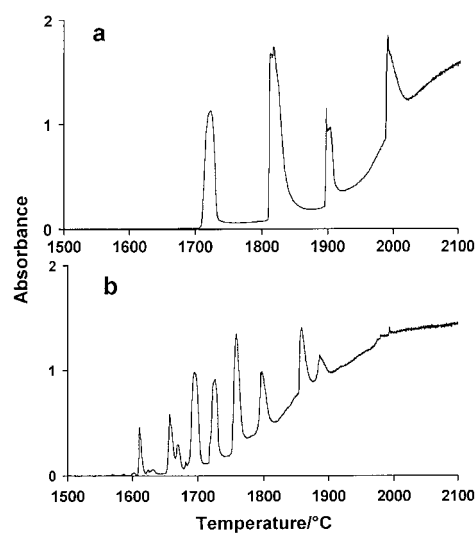


Fig. 4 Absorption profiles for 0.5 µg Yb evaporated at a heating rate 18 K s^{-1} in a THGA tube into Ar (a) and N_2 (b) atmospheres (50 ml min^{-1}).

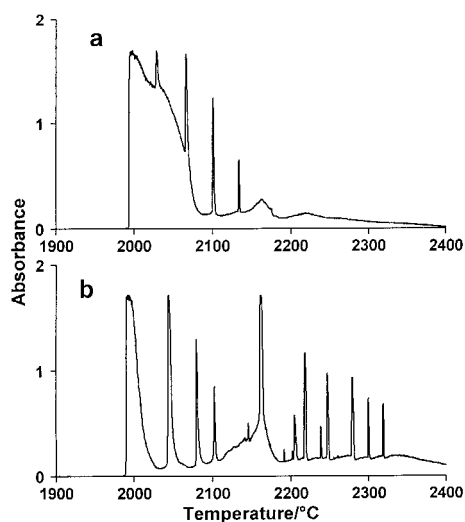


Fig. 5 Absorption profiles for 2.5 µg Al evaporated at a heating rate 12 K s^{-1} in a THGA tube into a N_2 atmosphere (50 ml min^{-1}): (a) 3 µl and (b) 30 µl aliquots injected.

Effect of flow rate of sheath gas. Fig. 6 illustrates the effect of flow rate of sheath gas on temporal oscillations. Higher rates, irrespective of other parameters, promote an increase in the number and width of oscillations. An identical trend was obtained for Mn and Yb. This may be connected to the reduced concentration of gaseous carbides in the reaction zone, which determines the rate of reaction and density of the carbon film on the surface of oxide particles. Reducing either of these parameters could result in deceleration of the autocatalytic reaction and a shortening of the intervals between adjacent spikes, respectively.

Effect of Sr addition. The addition of Sr greatly stimulates temporal oscillations in the process of carbothermal reduction of Al, Yb and Mn oxides, as illustrated by the data for Al and Mn in Figs. 7 and 8. This effect is most pronounced for Mn; instead of the one spike noticed in the absence of Sr, more than 10 spikes are observed with the addition of 5 µg of Sr. The same stimulation of oscillations for Al and Mn was observed in non-isothermal HGA tubes.¹ This effect may be due to formation of gaseous molecules of SrC_2 and their participation in (or initiation of) the reduction of Al, Mn and Yb oxides. A high concentration of SrC_2 molecules was reported by Prell *et al.*⁷ in

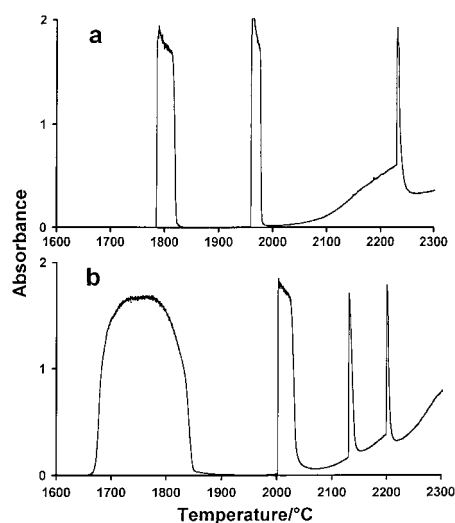


Fig. 6 Absorption profiles for 13 µg Al evaporated at a heating rate 14 K s^{-1} in a THGA tube into an Ar atmosphere: (a) 0 and (b) 250 ml min^{-1} .

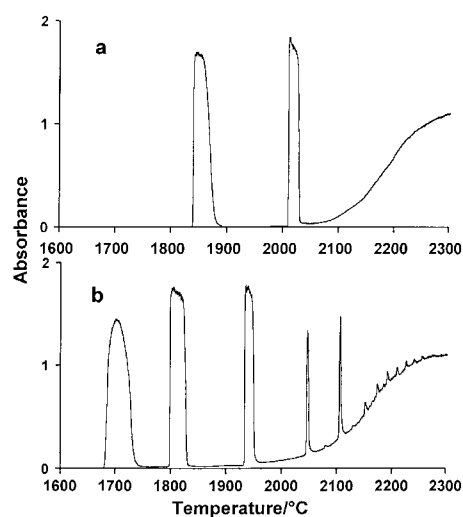


Fig. 7 Absorption profiles for 4 µg Al evaporated at a heating rate 14 K s^{-1} in a THGA tube into an Ar atmosphere (50 ml min^{-1}): without (a) and with (b) addition of 5 µg Sr.

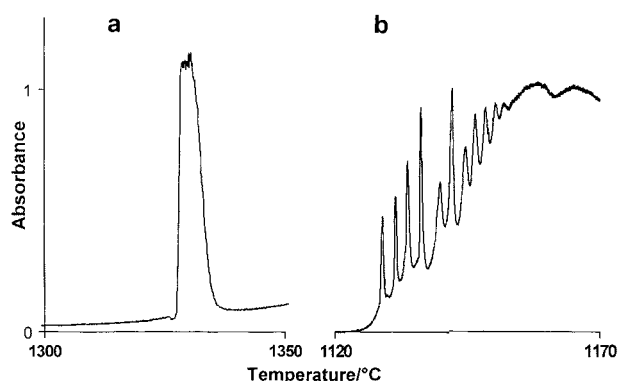


Fig. 8 Absorption profiles for 5 µg Mn at a heating rate 1 K s^{-1} in a THGA tube into an Ar atmosphere (250 ml min^{-1}): without (a) and with (b) addition of 5 µg Sr.

their mass-spectrometric studies of the evaporation of 50 ng of Sr (as its nitrate) in a graphite tube in an atmosphere of N_2 . They found the maximum concentration of SrC_2 at temperatures in the vicinity of 300 and 2000°C . In the range $800\text{--}1700^\circ\text{C}$, the concentration of carbides was very low. As the amount of Sr in the present experiments was 100-fold greater than that used by Prell *et al.*⁷, the presence of SrC_2 molecules may be expected at temperatures typical for the reduction of not only Al and Yb oxides ($1700\text{--}2300^\circ\text{C}$) but for that of Mn oxide ($1100\text{--}1400^\circ\text{C}$) as well.

Spatially non-isothermal tube

Figs. 9–12 present temporal oscillations for Al_2O_3 and Yb_2O_3 , respectively, for samples evaporated from the platform under different modes of heating. Figs. 9 and 11 illustrate the evaporation profiles for continuous (a) and interrupted (b and c) heating without removing the platform from the tube. Interruption of the heating process has not introduced any significant changes into either the distribution or number of spikes. The same results were observed when experiments were repeated with the addition of an intermediate stage of removal of the platform and heating of the empty tube [Figs. 10(c) and 12(c)]. It can be seen that, for both elements, there is a slowly rising, broad signal (more pronounced for Yb) which is the result of condensation of sample vapours onto the tube wall caused by the first several spikes at the stage “b”. However, this signal is connected with thermal dissociation of oxides. In no

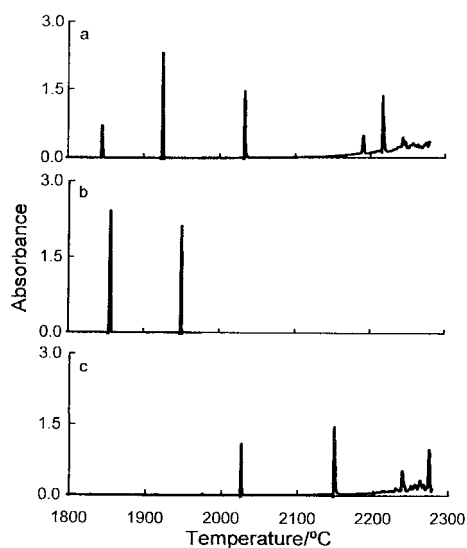


Fig. 9 Absorption profiles for 6 µg Al evaporated from the platform at a heating rate 10 K s^{-1} in an HGA tube into an Ar atmosphere (300 ml min^{-1}): (a) 1700–2300 °C (without interruption); (b) 1700–1980 °C (heating was interrupted after the second spike); and (c) 1700–2300 °C (heating resumed after interruption).

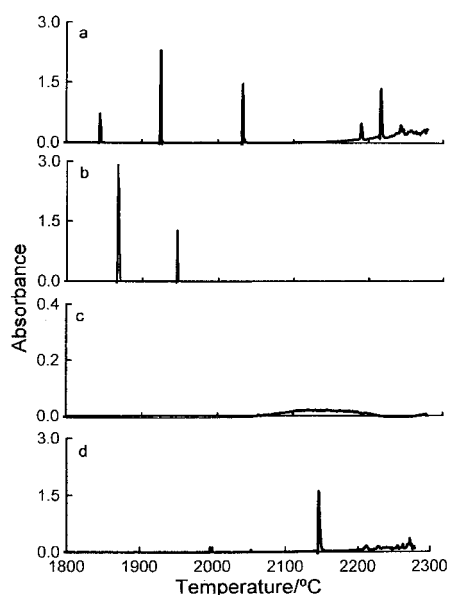


Fig. 10 Absorption profiles for 6 µg Al evaporated from the platform at a heating rate 10 K s^{-1} in an HGA tube into an Ar atmosphere (300 ml min^{-1}): (a) 1700–2300 °C (without interruption); (b) 1700–1970 °C (heating was interrupted after the second spike and the platform was removed); (c) 1700–2300 °C (repeated heating of the empty tube); and (d) 1700–2300 °C (the platform was re-inserted and the heating repeated).

case, during several tens experiments, was there an appearance of fast rising peaks (spikes) at this stage.

Furthermore, as can be seen from Figs. 10(d) and 12(d), the intermediate stage “c” did not affect the character of spikes generated during the final stage of heating. This implies that the only source for the temporal oscillations is the primary site of sample deposition on the platform. The reason for such “inert” behaviour toward subsequent reduction of these oxides condensed on the wall is their homogeneous distribution on the surface in the form of particles smaller in size than necessary for the autocatalytic process of oxide reduction.² Only in the case of extremely high concentrations of sample vapours, as in experiments reported by Lamoureux *et al.*,⁴ or

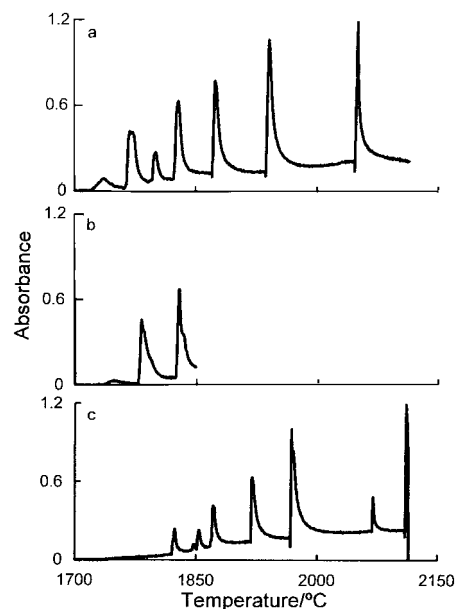


Fig. 11 Absorption profiles for 4 µg Yb evaporated from the platform at a heating rate of 9 K s^{-1} in an HGA tube into an Ar atmosphere (300 ml min^{-1}): (a) 1700–2300 °C (without interruption); (b) 1700–1860 °C (heating was interrupted after the second spike); and (c) 1700–2300 °C (heating resumed after interruption).

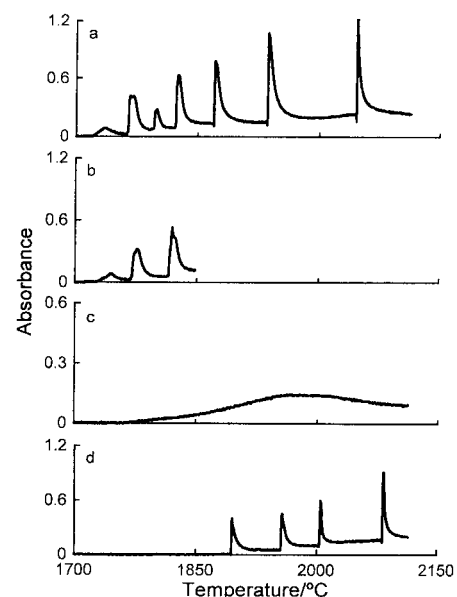


Fig. 12 Absorption profiles for 4 µg Yb evaporated from the platform at a heating rate 9 K s^{-1} in an HGA tube into an Ar atmosphere (300 ml min^{-1}): (a) 1700–2300 °C (without interruption); (b) 1700–1860 °C (heating was interrupted after the second spike and the platform was removed); (c) 1700–2300 °C (repeated heating of the empty tube); and (d) 1700–2300 °C (the platform was re-inserted and the heating repeated).

transport of sample from wall to platform (under a high temperature gradient), as in the experiments by Ohlsson *et al.*,³ does the particle size of the condensed oxides reach a critical value necessary for initiation of autocatalytic reactions.

Conclusions

Observations of temporal signal oscillations during the evaporation of Al, Mn and Yb oxides in spatially isothermal THGA tubes have shown that practically all the features of this

phenomenon are similar to those occurring in spatially non-isothermal tubes. Under optimised conditions, up to 10–25 spikes could be observed for Mn. However, the number of oscillations from Al oxide in Ar in THGA tubes is typically smaller than that in non-isothermal HGA tubes. This may be connected with some differences in the characteristics of the pyrolytic graphite coating in THGA tubes and the solid pyrolytic graphite used for the manufacture of platforms for HGA tubes.

The results of this investigation into the possible effects of sample redistribution in non-isothermal tubes on such temporal oscillations are in complete agreement with these observations. No influence of evaporation/condensation processes on the temporal oscillations under common conditions of sampling and heating (and a high internal flow of sheath gas) could be discerned. These results suggest that the major source of such temporal oscillations is the primary sample residue. At the same time, the results described by Lamoureux *et al.*⁴ and by Ohlsson *et al.*,³ which appear to contradict this conclusion, have been interpreted. All the above support the gaseous carbide mechanism of formation of temporal oscillations.²

Acknowledgements

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References

- 1 B. V. L'vov, A. A. Vasilevich, A. O. Dyakov, J. W. H. Lam and R. E. Sturgeon, *J. Anal. At. Spectrom.*, 1999, **14**, 1019.
- 2 B. V. L'vov, L. K. Polzik, N. P. Romanova and A. I. Yuzefovskii, *J. Anal. At. Spectrom.*, 1990, **5**, 163.
- 3 K. E. Ohlsson, E. Iwamoto, W. Frech and A. Cedergren, *Spectrochim. Acta, Part B*, 1992, **47B**, 1341.
- 4 M. M. Lamoureux, C. L. Chakrabarti, J. C. Hutton, A. Kh. Gilmudinov, Yu. A. Zakharov and D. C. Grégoire, *Spectrochim. Acta, Part B*, 1995, **50B**, 1847.
- 5 B. V. L'vov, *Spectrochim. Acta, Part B*, 1989, **44B**, 1257.
- 6 B. V. L'vov, *Spectrochim. Acta, Part B*, 1996, **51B**, 533.
- 7 L. J. Prell, D. L. Styris and D. A. Redfield, *J. Anal. At. Spectrom.*, 1990, **5**, 231.

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