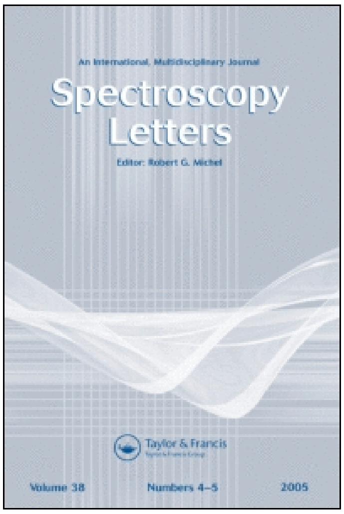

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Comparative Study of Ruthenium, Rhodium and Palladium as Chemical Modifiers in Graphite Furnace Atomic Absorption Spectrometry

Dimiter L. Tsalev[a]; Vera I. Slaveykova[a]
[a] Faculty of Chemistry, University of Sofia, Sofia, BULGARIA

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COMPARATIVE STUDY OF RUTHENIUM, RHODIUM AND PALLADIUM AS CHEMICAL MODIFIERS IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

KEY WORDS: Atomic Absorption Spectrometry, Electrothermal Atomization, Graphite Furnace, Chemical Modification, Ruthenium, Rhodium, Palladium, Ascorbic Acid.

DIMITER L. TSALEV AND VERA I. SLAVEYKOVA
Faculty of Chemistry, University of Sofia,
1 Anton Ivanov Blvd., Sofia 1126, BULGARIA

ABSTRACT

Comparative study on the efficiency of ruthenium, rhodium and palladium as chemical modifiers for thermal stabilization of 18 analyte elements with high and moderate volatility has been performed. Addition of ascorbic acid provided higher temperatures of thermal pretreatment by +50 to +250°C for the analytes: As, Ge, P, Pb, Se, Sn and Tl, as well as better performence for Ga, In and Tl. Possible mechanisms and trends in stabilization are discussed.

INTRODUCTION

The aim of this work was to evaluate and compare a series of chemical modifiers - Ru, Rh and Pd - as thermal stabilizers in electrothermal atomization atomic absorption spectrometry (ETA-AAS). Palladium is known as one of the most efficient and universal modifiers and has been a subject of numerous studies and analytical applications.[1-3] There has been only a limited number of papers on rhodium[4-8] (with Se,[4-6] Te,[7] and Sb[8] analytes) and on ruthenium modifiers.[8] Earlier, Dahl et al.[8] have compared the thermal stabilization of ^{125}Sb by five noble metal modifiers: Ir, Ru, Rh, Pt and Pd, as well as by a mixed "noble metal modifier" (0.03 % of each metal + ascorbic acid), the latter exhibiting the highest efficiency.

A comparative study on the series of the modifiers (Ru-Rh-Pd) seemed well grounded because while their mode of action should be similar, still their volatility differs substantially (Pd > Ru > Rh). Hence comparing their efficiency towards numerous analytes with different volatility and reactivity pattern could help in better understanding the role of physico-chemical parameters on mechanisms and effects of noble metal modifiers.

TABLE 1

Temperature Program I
for the HGA-400 Heated Graphite Atomizer

Parameter	Step				
	1	2	3	4	5
Temperature (°C)	130	300	var[a]	var[b]	2650
Ramp time (s)	15	10	10	0	1
Hold time (s)	10	10	30	3-4	3
Read (s)	-	-	-	*	-
Ar flow (ml/min)	300	300	300	0[c]	300

[a] see Table 3;

[b] Zn 1400°C; Cd 1600°C; Ag, Au, Bi, In, Pb, and Tl 2000°C; Cu, and Mn 2200°C; As, Ga, Sb, Se, Sn and Te 2400°C; Ge 2500°C; P 2600°C;

[c] 300 ml/min for Zn.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 2380 G atomic absorption spectrometer equipped with a HGA-400 graphite furnace and deuterium background corrector was used. The operating parameters were set as recommended by the manufacturer except that a bandpass of 2 nm and alternate wavelengths were used for Bi (306.8 nm), Sb (231.2 nm)

TABLE 2

Alternative Temperature Program (Program II) for Some Experiments with Ga, In and Tl

Parameter	Step							
	1	2	3	4	5	6	7	8
Temperature (°C)	300	900	30	120	300	var$^{\alpha}$	2200	2500
Ramp time (s)	15	10	10	15	10	10	0	1
Hold time (s)	30	30	15	10	10	30	3	2
Read (s)	-	-	-	-	-	-	*	-
Ar flow (ml/min)	300	300	0	300	300	300	0	300

$^{\alpha}$ Variable between 400 and 1400°C

and Sn (286.3 nm). Uncoated graphite tubes and peak-height mode of measurements were used throughout. The standard temperature program for the HGA-400 is shown in Table 1. In some experiments with Ga, In and Tl analytes was also used an alternative temperature program as shown in Table 2 (Program II). The latter program assured longer pretreatment times up to 900°C or pre-treatment of modifier with subsequent injection of an analyte aliquot during the intermediate "cool-down" Step 3. Twenty-μl aliquots of analyte solution were followed by injection of 10-μl portions of the reductant, 1 % m/v ascorbic acid (manual injections by means of Eppendorf pipettes).

Reagents

All solutions were prepared from analytical grade reagents in doubly-distilled water (from an all quartz still). Stock standard solutions of Ru, Rh and Pd, 1000 μg/ml, in 10 % HCl (Aldrich Chemical Company) were diluted as required and used as chemical modifiers. In some experiments with Ga, In and Tl was also used palladium modifier in a nitrate form (0.1 % m/v Pd(II) as nitrate in 15 % HNO_3, E. Merck). Ascorbic acid solution, 1 % m/v was prepared daily.

RESULTS AND DISCUSSION

Thermal pretreatment curves have been plotted for all 18 analytes in the presence of Pd, Rh and Ru as chlorides; from these curves were derived the maximum thermal pretreatment temperatures (T_{max}) which are compiled in Table 3. For comparison are also given the corresponding temperatures in the absence of modifiers. Several trends are revealed on examining Table 3. All these modifiers are efficient and rather universal thermal stabilizers of volatile analytes. Particularly efficient is the stabilization of As, Au, Ge, P, Sb, Se, Sn and Te ($\geq$ 1200°C).

TABLE 3

Maximum Temperatures of Thermal Pretreatment

Analyte	Pretreatment temperature (°C)						
	Without modifier[a]	Ru	Ru+A	Rh	Rh+A	Pd	Pd+A
Ag	500	900	900	900	900	950	950
As	900[a]	1250	1500	1250	1300	1300	1200
Au	600[a]	1100	1300	1100	1100	1300	1100
Bi	400	1100	1100	1100	1000	1200	1000
Cd	250	700	700	600	700	550	650
Cu	900	1050	1100	1100	1100	900	1000
Ga	800[b]	1200	1050	1200	1000	1150	1200
Ge	800[c]	1200	1250	1100	1200	1200	1200
In	800	1100	1200	1200	1200	1250	900
Mn	1000	1100	1100	1100	1250	1250	1300
P	1400[a]	1400	1500	1200	1400	1200	1300
Pb	500	950	1000	950	1000	1050	1100
Sb	1000[a]	1300	1200	1300	1250	1300	1350
Se	200	1250	1350	1250	1350	1250	1300
Sn	900[a]	1150	1300	1150	1450	1150	1350
Te	600	1100	1350	1100	1350	1150	1250
Tl	400[a]	900	1100	900	900	900	800
Zn	400[a]	750	900	800	900	900	900

[a] Uncoated tubes and 0.2% HNO_3 diluent except for the analytes: As (3% H_2SO_4), Au (0.2% HCl), P (20 μg La as $La(NO_3)_3$), Sb (0.3% H_2SO_4), Sn (3% HNO_3+10% NH_3), Tl (0.5% HNO_3), and Zn (H_2O) (From Ref. 9);

[b] Pyro-coated tube (Ref. 10); [c] From Ref. 10;

4 μg Ru, Rh or Pd; +A: 200 μg ascorbic acid added.

Noteworthy is the effect on heavier analytes like Au, Bi, Pb and Te which are among the elements not well stabilized by most known chemical modifiers.[2] For many analytes there is no major difference between the action of the three modifiers; e.g. for As, Ag, Cu, Ge, In, Sb, Sn, Te and Tl the maximum pretreatment temperatures are the same (± 50°C) with all three modifiers.

The effect of the mass of modifier (0.4 to 20 μg) on several analytes representing different groups of volatile analytes:[2,11] Au, Pb, Se and Sn is shown in Fig. 1. The T_{max} reach a plateau at rather small amounts of modifiers (1 μg for Sn, 2 μg for Au and Pb, and 4 μg for the most volatile analyte - Se).

Most analyte elements are tolerable to an excess of chloride introduced by the Cl^- form of modifiers. Exceptions are the elements of the III A group of the Periodic Table: Ga, In and Tl. With these analytes is observed depression of the signal at low thermal pretreatment temperatures as demonstrated on Fig. 2 and 3 (open circles). The depression follows the trends: Ga > In ~ Tl and Ru > Rh > Pd. It is eliminated when the modifier is introduced in a nitrate form (Fig. 3-c) or when appropriate, alternative pretreatment modes and programs are applied (Fig. 2(●), Fig. 3-a(●) and Fig. 3-b). These alternative programs (Program II from Table 2) assure a thermal pretreatment of the injected

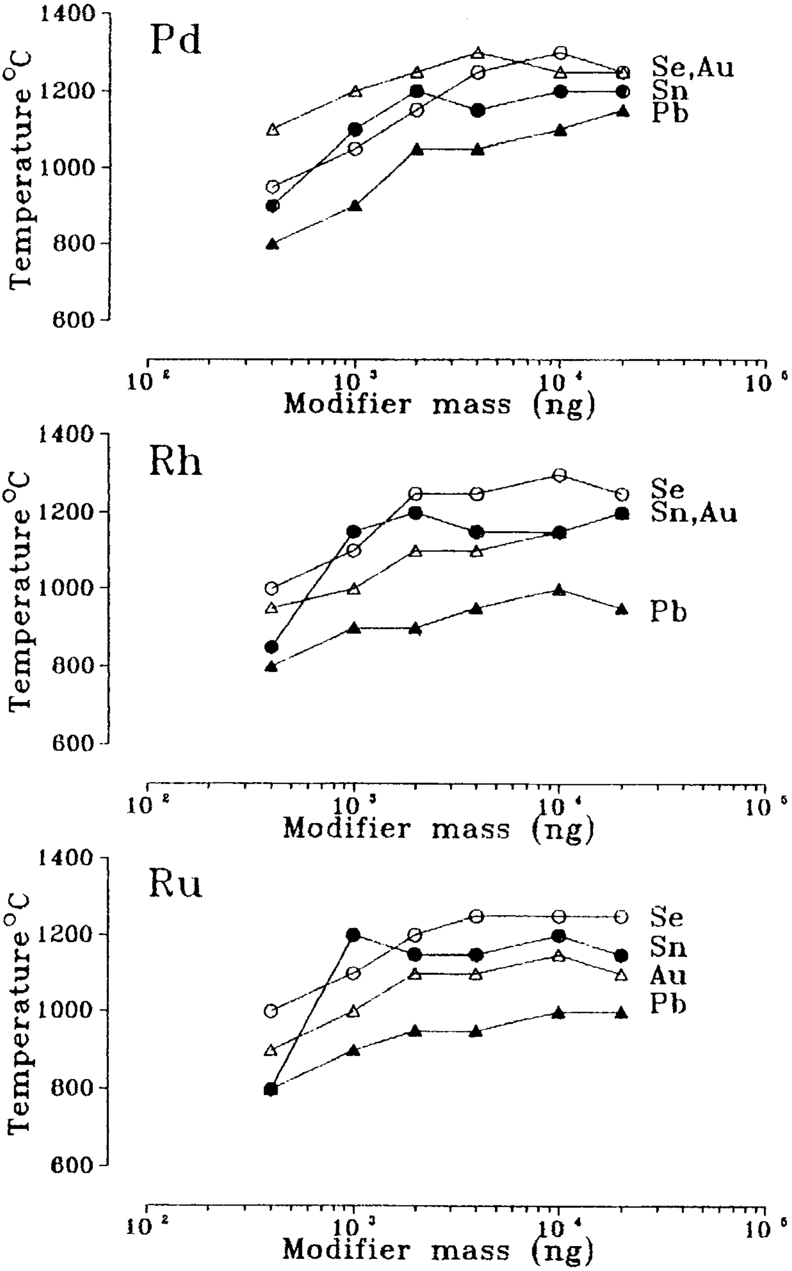

FIG. 1. Effect of modifier mass on maximum pretreatment temperature. 4 μg Pd, Rh or Ru added.

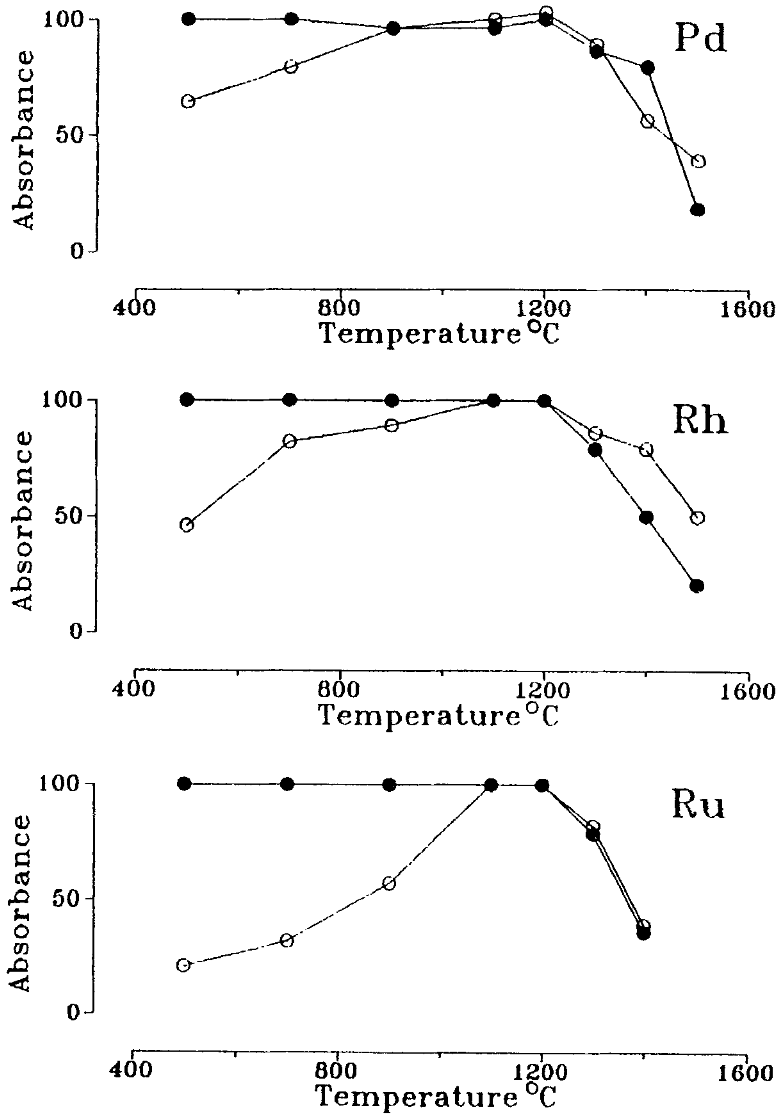

Fig. 2. Thermal pretreatment curves for gallium in the presence of 4 μg of Pd, Rh or Ru as chlorides (o) Program I; (●) Program II.

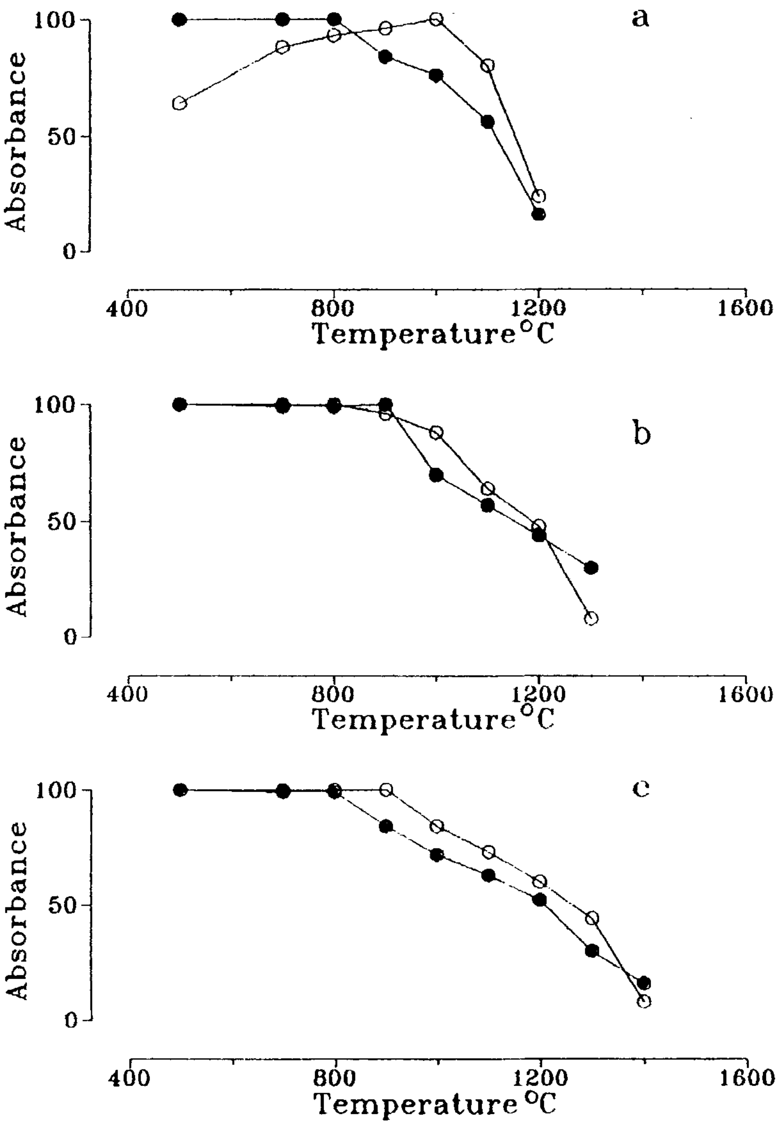

FIG. 3. Thermal pretreatment curves for thallium in the presence of 4 µg of Pd as a chloride (a,b) or nitrate (c), with different pretreatment modes as detailed in text.

modifier up to 900°C so as to eliminate the chloride, with subsequent injection of sample aliquot during Step 3 (Fig. 2(●), Fig. 3-b(●). Alternatively, longer thermal pretreatment to 900°C could help in transforming the modifier into an active form (Fig. 3-a(●)) or else the modifier could be reduced early in the temperature program by adding reductant - 200 μg ascorbic acid (Fig. 3-b(o)).

One could expect that gallium, indium and thallium are more vulnerable to the depression by chloride because of the high bond energies of these elements with chlorine (>400 kJ/mol; GaCl > InCl > TlCl).[12] Chloride and oxide species of these analytes are relatively difficult to reduce early in the temperature program. On the other hand, the modifier by itself "stabilizes" the chloride up to 700-900°C until chlorides are thermally decomposed (Table 4).

Analytical performance of noble metal modifiers in the presence of chloride is of practical importance since many real matrices/digests may contain excess of Cl^- or HCl. Experimental results show that palladium modifier is less prone to chloride interference as compared to Rh and Pd. Calculations of the Gibbs free energy change show that the thermal decomposition of chlorides should be thermodynamically feasible above 800°C for $RuCl_3$ and $RhCl_3$ and above 900°C for $PdCl_2$

TABLE 4

Selected Data for Pd, Rh and Ru

Parameter	Element		
	Pd	Rh	Ru
Melting point, °C (Ref. 12)	1554	1965	2310
T_{max}, °C[a]	1100	1400	1400
T_{app}, °C[a]	1500	1850	1900
T_d , °C[b]	675-755	800-880	650-740

[a] T_{max}: max. temperature of thermal pretreatment;[13]
T_{app}: appearance temperature; in 0.2 % HNO_3;[13]

[b] T_d : decomposition temperature of chlorides (initial-final temperature), by XRD, TG and DTA.[14,15]

at partial pressure of Cl_2 1 atm, but these temperatures could be as low as 270°C at $p(Cl_2) \sim 10^{-2}$ atm. Anyway these temperatures are much higher than those for the thermal decomposition or reduction of modifier *oxides*. Experimental results of Kamiya et al.[14,15] on thermal decomposition of chlorides of Ru,[14] Rh,[15] and Pd[15] by TG, DTA and XRD indicate on transformation intervals of 650-880°C (Table 4).

Thus an effect of residual chloride on analyte stabilization and atomization should be expected; this effect might well be superimposed on other effects of modifiers, e.g. on those effects caused by differences in their volatility and reactivity (Table 4). Such complexity could account for the lack of clear trends in thermal stabilization within the series Ru-Rh-Pd in the absence of reductant. Let us note that the volatility follows a simple trend (Pd > Rh > Ru) but the catalytic properties[16] and chemical reactivity are rather ranked in the oposite direction.

It is a common opinion in ETA-AAS that palladium should be reduced early in temperature program in order to assure metallochemical interaction with analyte elements.[17-19] Addition of reductant like hydroxylamine hydrochloride, ascorbic acid or Ar + H_2 has proved very efficient in reducing to highly dispersed and reactive metallic form,[18,19] particularly in the presence of halides as well as with certain analytes (Tl, Pb).[19]

In the presence of 200 μg of ascorbic acid the temperatures of thermal pretreatment are the same or higher by +50 to +250°C, particularly with volatile analytes As, Ge, P, Pb, Se, Sn and Tl (Table 3 and Fig. 4). Addition of ascorbic acid should be able to assure an early reduction of modifier to a highly dispersed metallic form and thus to separate the noble metal from its counterpartner, the chloride. On thermal decomposition of ascorbic acid are produced efficient reductants such as C, CO and H_2;[20] thus elimination of Cl^- as HCl and reduction of analyte species are promoted.

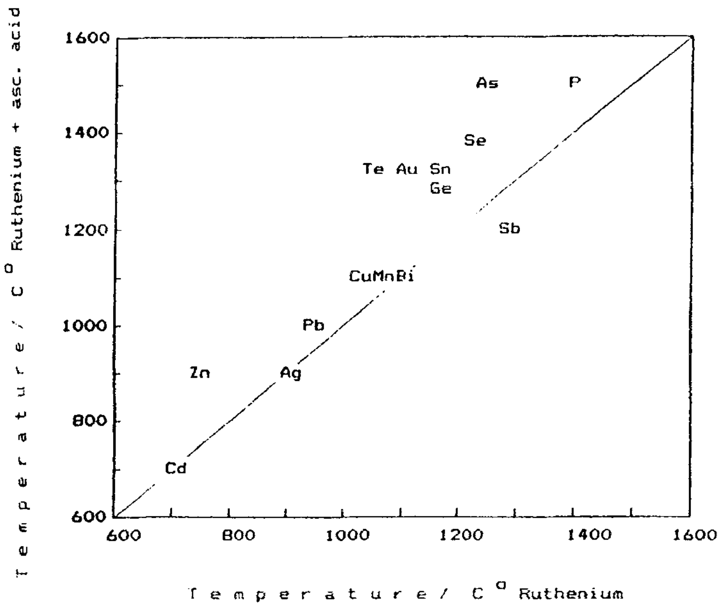

FIG. 4. Maximum thermal pretreatment temperatures in the presence of Ru + ascorbic acid versus Ru. 4 μg Ru as a chloride; 200 μg ascorbic acid.

Volynsky et al.[16] refer also to the catalytic effect of metallic palladium on low temperature reduction of analyte oxides. Many elements are able to form compounds and solid solutions with noble metals, as sumarized in Fig. 5 on the basis of data from Kornilov et al.[21] Some of these analyte-palladium bonds[22,23] and crystallographic phases[24,25] have been observed experimentally by instrumental methods.

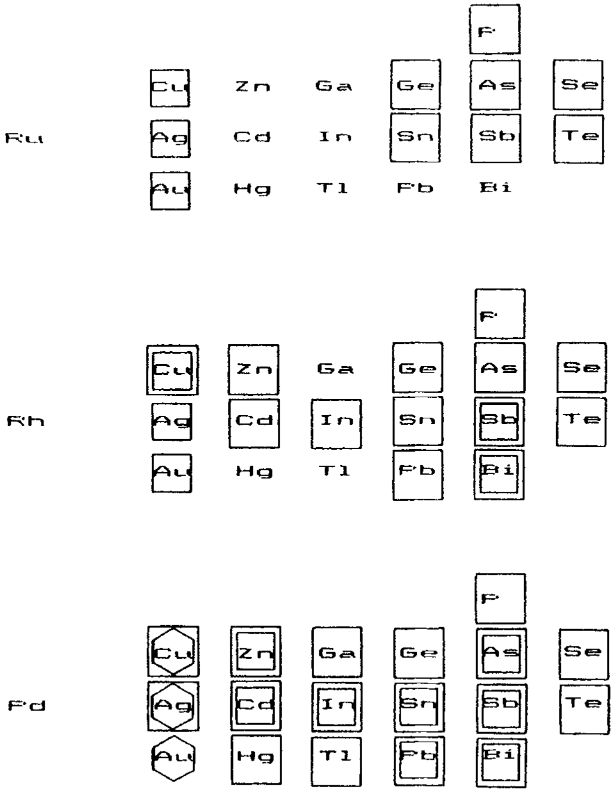

FIG. 5. Literature data on formation of continuous solid solutions (hexagons), solid solutions with limited solubility (small squares) and compounds (large squares).

In the presence of reductant there are more clear trends in T_{max} versus melting points of modifiers, generally in the series Ru > Rh > Pd. This trend is illustrated in Fig. 6 with the analytes As, Ge, In, P, Se, Te and Tl. These analytes exhibit relatively high

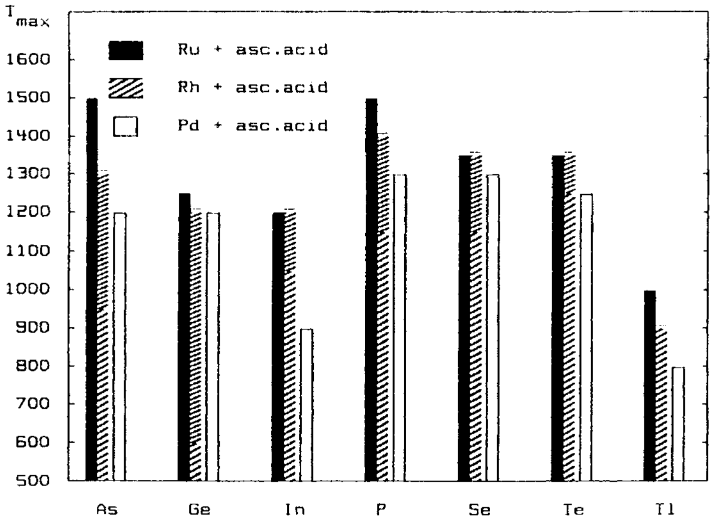

FIG. 6. Trends in the maximum pretreatment temperatures in the presence of Ru-Rh-Pd series of chemical modifiers. 4 μg Ru, Rh or Pd, 200 μg asc.acid.

electronegativity and tend to form strong chemical bonds: analyte-noble metal modifier. It could be expected that Ru and Rh provide more thermally stable matrix for the stabilization of intermetallic phases and thus can better stabilize these analytes as compared with palladium modifier. Therefore such refractory "cocktails" of several noble metals, containing even less volatile components like Ir and Pt, could much better stabilize volatiles than single-component modifiers (e.g. as observed by Dahl et al.[8] with Sb).

CONCLUSION

Ruthenium, rhodium and palladium series of chemical modifiers are highly efficient and universal thermal stabilizers for a number of volatile analytes, except for Cd and Zn. In the absence of reductant, there is no distinct trend in thermal stabilization pattern of these modifiers. In the presence of ascorbic acid, the maximum pretreatment temperatures are similar or higher by +50 to + 250°C for most volatile analytes. The efficiency of stabilization could be ranked in the order Ru > Rh > Pd for a group of analytes: As, Ge, In, P, Se, Te and Tl.

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