Chinese Chemical Letters Vol. 10, No. 4, pp. 333–334, 1999

Investigation on the Thermostability of Germanium and Elimination of Chloride and Sulfate. Interference on Germanium in Graphite Furnace Atomic Absorption Spectrometry

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Abstract: The thermostability and the interference-resisting property of germanium (Ge) in graphite furnace atomic absorption spectrometry (GF.AAS) were increased remarkably when palladium and lithium nitrates were used as complexing matrix modifiers and barium nitrate as supplementary matrix modifier.

Keywords: GF.AAS, germanium, eliminate interference.

The advantage of determination of trace Ge by GF.AAS is that only a few microliters of sample is used. But the matrix interference,especially chloride ion and sulfate ion is very serious[1]. So there is an important subject for further investigating to eliminate these interferences.

Nitric acid is an oxidant. The tetravalent Ge is stabilized owing to its oxidation . The magnitude of the Ge signal varies with the concentration of nitric acid and the maximum of the Ge signal is observed with 0.6 mol/L nitric acid. The action of some nitrates is similar but the concentration of various nitrates is different when the maximum of the Ge signal is observed. The influence of monovalent nitrate salts on the Ge signal is smaller than that of bivalent nitrate salts at the same concentration. The best result is found with palladium nitrate at 8.0×10^{-3}mol/L. The sensitivity of Ge signal is about twenty times higher than that without palladium nitrate. The thermostability of Ge is closely related with the matrix coexisting elements. It is found that in the presence of nitric acid or/and nitrate higher ashing temperature can be used. Ashing temperature up to 700℃ is possible without any loss of Ge in 0.6 mol/L nitric acid. The thermostability of Ge is raised with various nitrates. It also changes with the amount of nitrate. The influence of species and the amount of nitrate are shown in the following **Table**: Ge can be stabilized by M^{+} and M^{++} of nitrate owing to the formation of stable compounds. The ashing products of Ge in various systems are determined by x-ray diffraction spectrometry. The ashing product is GeO_2, $Na_2O.GeO_2$, NiO. G_2O_2, or PdO. GeO_2, respectively as the ashing temperature is up to 700℃. The ashing product of Ge in the system of nitric acid and palladium nitrate is Ge-Pd intermetallic compound as ashing

temperature up to 1200℃. So the reaction mechanism, the thermostability, the determination sensitivity and the interference-resisting property of Ge are different in various systems.

Table 1. The influence of species and amount of nitrate

Species	Amounts(mol/L)	Temp(℃)
$NaNO_3$	0.1	800
$LiNO_3$	0.1	900
$Ni(NO_3)_2$	1.2×10^{-2}	1000
$Ba(NO_3)_2$	1.2×10^{-2}	1200
$Pd(NO_3)_2$	8.0×10^{-4}	800
$Pd(NO_3)_2$	1.6×10^{-3}	1000
$Pd(NO_3)_2$	1.2×10^{-2}	1200
$Pd(NO_3)_2$,$LiNO_3$	1.2×10^{-2},0.1	1600

The chloride ion interference on Ge is caused by volatilizaton of $GeCl_2$ in the ashing stage and sulfate ion interference is caused by the formation of the thermally stable GeS in the gas phase during the atomization stage[2,3]. It was found that nitric acid not only stabilized Ge thermally but also expelled Cl^{-1} from the system, so that the interference of chloride ion is inhibited. If palladium nitrate is coexistent the more stable intermetallic compound of Ge-Pd can be formed and the ashing temperature can be raised to 1200℃. So The interference of chloride ion can be eliminated more efficiently. The experimental results indicate that the range of interference-free determination is increased up to 6.0 mg/mL NaCl. But the interference of sulfate ion can not be eliminated. We found that a mixture of palladium nitrate and lithium nitrate results in a higher tolerance for interference compared to palladium nitrate alone. The interfering concentration of Na_2SO_4 permit to 80 μg/mL in 0.6 mol/L HNO_3, 0.1 mol/L $LiNO_3$ and 1.2×10^{-2} mol/L $Pd(NO_3)_2$ medium and ashing temperature is raised to 1400℃. By the addition of 2.0 mg/mL barium nitrate as a supplementary chemical modifier the range of interference-free determination is further increased to 600 μg/mL Na_2SO_4.

The method described above has been used to determine Ge in some biological samples. The standard recovery is between 93-107%. The linear range of determining concentration is 0.02-0.60 μg/mL Ge. The detection limit is 0.01 μg/mL Ge and the relative standard deviation is ±4.7%for 20 determinations of 2.0 μg/mL Ge.

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Received 30 November 1998