Determination of Silicon in Tantalum and its Compounds Using ICP-OES

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Received 4 November 2002

Determination of trace levels of silicon in tantalum hydroxide, potassium tantalum fluoride, and tantalum powder using inductively coupled plasma optical emission spectrometer is presented. The main limitation for the analysis of silicon is its volatility, a high risk of contamination, and its presence in hydrofluoric acid which causes a lot of difficulties in line selection and thereby analysis. Here, a novel process was applied for line selection using cupferron for partial precipitation of tantalum for selecting tantalum interference-free silicon line. Preparing samples in clean room controlled the contamination caused by silicon. The results of silicon analyzed in clean room and in open room are also presented.

Tantalum and its compounds are dissolved in an acid mixture containing HF and HNO_3. Silicon has low solubility in acid media and the determination of silicon precisely by solution methods [1—4] is very difficult due to the high volatility of silicon tetrafluoride [5] which makes the direct methods [6, 7] of analysis best suited, as the sample preparation step is avoided. However, methods like direct current optical emission spectrometry (DCOES) and direct neutron activation do not show sufficient sensitivity. Another inherent goal for reliable performance of such a trace analysis is to improve silicon blank of the digested solutions. There is no reported literature available on determination of silicon in tantalum powder using inductively coupled plasma optical emission spectrometer (ICP-OES). An electrothermal atomic absorption spectrometer (ETAAS) with a transversely heated graphite tube and a solid sampling system based on the boat technique were used for the development of methods for direct determination of silicon [8] in powdered niobium pentoxide, titanium dioxide, and zirconium dioxide, where the matrix caused serious spectral and background interferences. Silicon [9] was also determined directly in nickel-based alloys by ETAAS at 251.611 nm, here also spectral interference from nickel and iron was found, and hence the pretreatment was done for removal of nickel and iron.

The main aim of this work is the determination of silicon directly in tantalum matrix without separation of the matrix, using 0.64 m monochromator ICP-OES. The main limitation is the selection of interference-free line of silicon from matrix element Ta. Tantalum is usually dissolved in HF media, which always contain silicon as impurity. Hence line identification was a major problem. Using cupferron reagent, by partially precipitating tantalum and thereby selecting tantalum interference-free silicon line, successfully solved this problem of line identification. Silicon content was precisely analyzed at every stage (Fig. 1) of the capacitor grade tantalum powder preparation process. Capacitor grade tantalum powder doped with silicon suppresses DC leakage current normally and also enhances capacitance, hence silicon is added at various stages of tantalum powder production, but is preferably, added during reduction of a tantalum precursor (K_2TaF_7 reduction by sodium).

EXPERIMENTAL

The instrument used for the analysis of silicon in tantalum and its compounds is ICP-OES (model JY-24R, Jobin Yvon, France). A cross-flow type of nebulizer was used for nebulization in the ICP-OES instrument. The instrumental parameters of the ICP-OES are given in Table 1. All operations were performed under class 100 laminar flow workbench situated in a metal-free clean room facility. Nitric acid used was of suprapure reagent grade (Merck, Germany), sulfuric acid of AR grade (Merck, India), hydrofluoric acid was of AR grade (Merck, India), and cupferron used was also of AR grade (H. T. Baker, India). Tantalum powder used for validation was STA-18KT (Si < 3 $\mu g\ cm^{-3}$, H. C. Starck GmbH &

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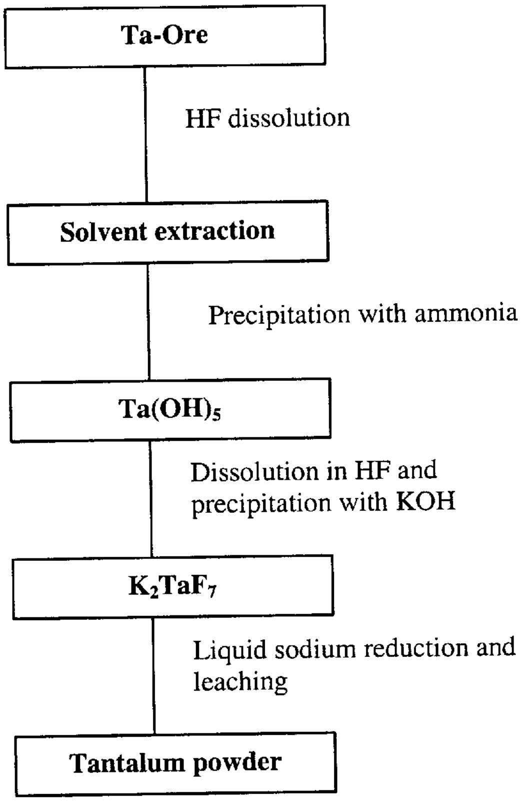


Fig. 1. Flow chart of tantalum powder preparation processes.

Table 1. ICP-OES Operating Conditions

Sequential spectrometer	
Spectrometer	Jobin Yvon JY-24R 0.64 m Czerny—Turner
Grating	Holographic, 3600 grooves mm^{-1}
Spectral range	160—500 nm
Slit width	20 nm for entrance and exits, adjustable
Plasma	
Plasma torch assembly	Fused quartz with capillary injection
Nebulizer and spray chamber	Cross-flow type nebulizer and teflon dual tube spray chamber
Argon nebulizer gas flow rate	0.4 dm^3 min^{-1}
Argon plasma gas flow rate	12 dm^3 min^{-1}

Co. KG, Germany) and FTW-100 (Si 10 μg cm^{-3}, China). The single elemental standard solutions were from Merck, Germany. The deionized water used was prepared using the Millipore system, France.

Sample Preparation

1 g of Ta(OH)$_5$/K$_2$TaF$_7$ was moistened in 5 cm^3 of water and dissolved in 3 cm^3 of HF. In the case of tantalum powder, 1 g was moistened with 5 cm^3 of water and dissolved in 3 cm^3 of HF and 1 cm^3 of HNO$_3$. All the samples were kept in a closed Teflon beaker without heating during dissolution and made up to 100 cm^3. For partial removal of tantalum matrix the solution of tantalum (1 mg cm^{-3}) was acidified with 1.5—2.0 M-H$_2$SO$_4$. The solution was then cooled to room temperature and aqueous cupferron [10] (10 cm^3, c = 0.5 g dm^{-3}) was added slowly with constant stirring until precipitation appeared.

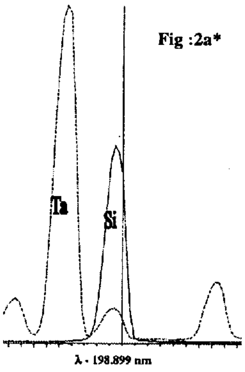
RESULTS AND DISCUSSION

Analytical lines were selected [11, 12] on the basis of investigation of spectral interferences of tantalum matrix on silicon. The spectral lines studied for silicon were 198.899 nm, 212.412 nm, 221.089 nm, 221.667 nm, 243.515 nm, 250.690 nm, 251.432 nm, 251.611 nm, 251.920 nm, 252.411 nm, 252.851 nm, and 288.158 nm. Two 1 mg cm^{-3} tantalum solutions were doped with 1 mg dm^{-3} silicon solution; one of them was precipitated by cupferron solution, which precipitates the matrix tantalum but not the silicon. Cupferron was not dissolved in alcohol but it was partially dissolved in water because alcohol causes disturbances in the plasma thereby causing errors in the analysis. The graphs are shown separately with and without addition of cupferron, from this it was observed that only the tantalum peak decreased whether it was directly or wing-overlapped with silicon line.

Table 2. Dissolution of Tantalum Powder in Open and Closed Vessels in Clean Room*

Sample	Open dissolution in clean room			Closed dissolution in clean room		
	Analyzed values ρ /(mg dm^{-3})	1 mg dm^{-3}doped recovery/%	5 mg dm^{-3}doped recovery/%	Analyzed values ρ /(mg dm^{-3})	1 mg dm^{-3}doped recovery/ %	5 mg dm^{-3}doped recovery/ %
FTW-100	6.50 ± 0.12	65.34 ± 0.25	78.16 ± 0.31	9.80 ± 0.18	98.34 ± 0.19	98.78 ± 0.18
STA-18KT	1.60 ± 0.10	58.59 ± 0.28	76.18 ± 0.42	2.83 ± 0.10	96.89 ± 0.22	97.80 ± 0.15

Note: All results are average of five readings.
*± SD of 5 readings.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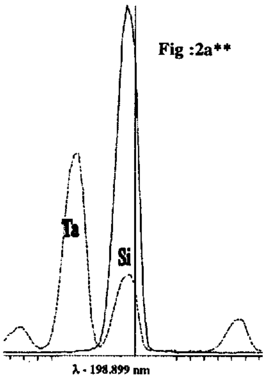
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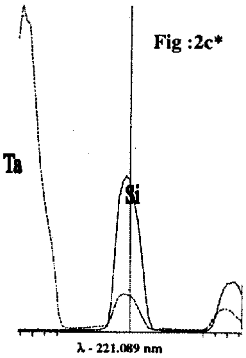
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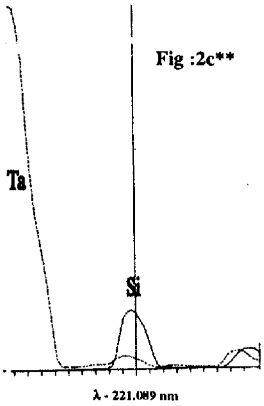
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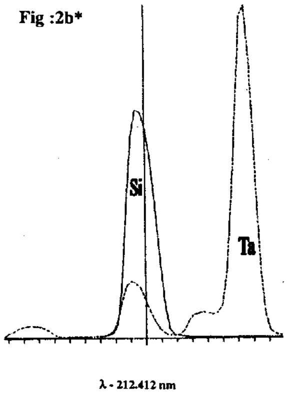
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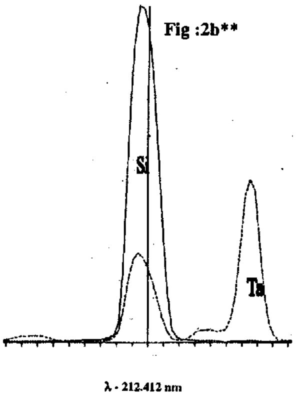
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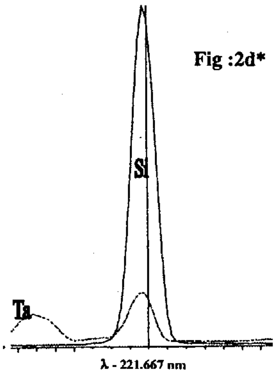
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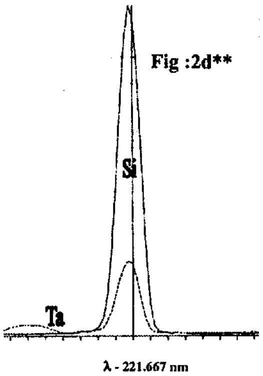
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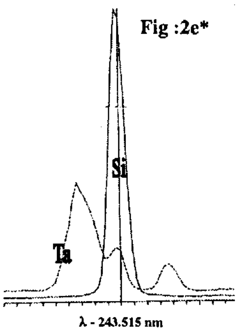
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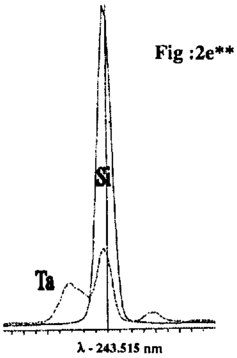
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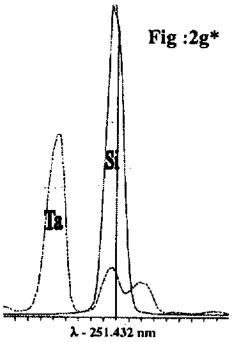
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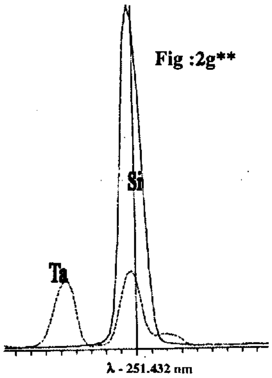
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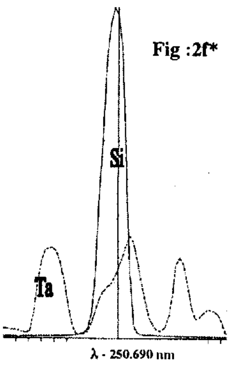
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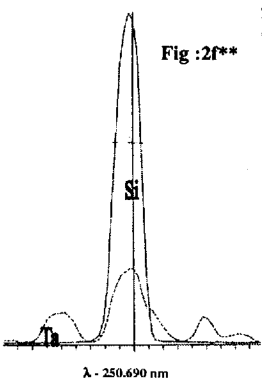
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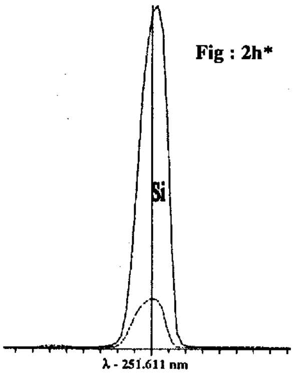
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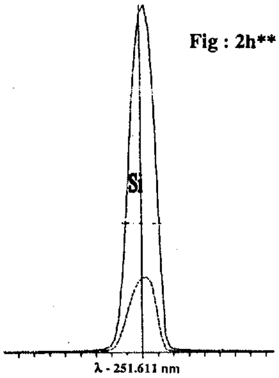
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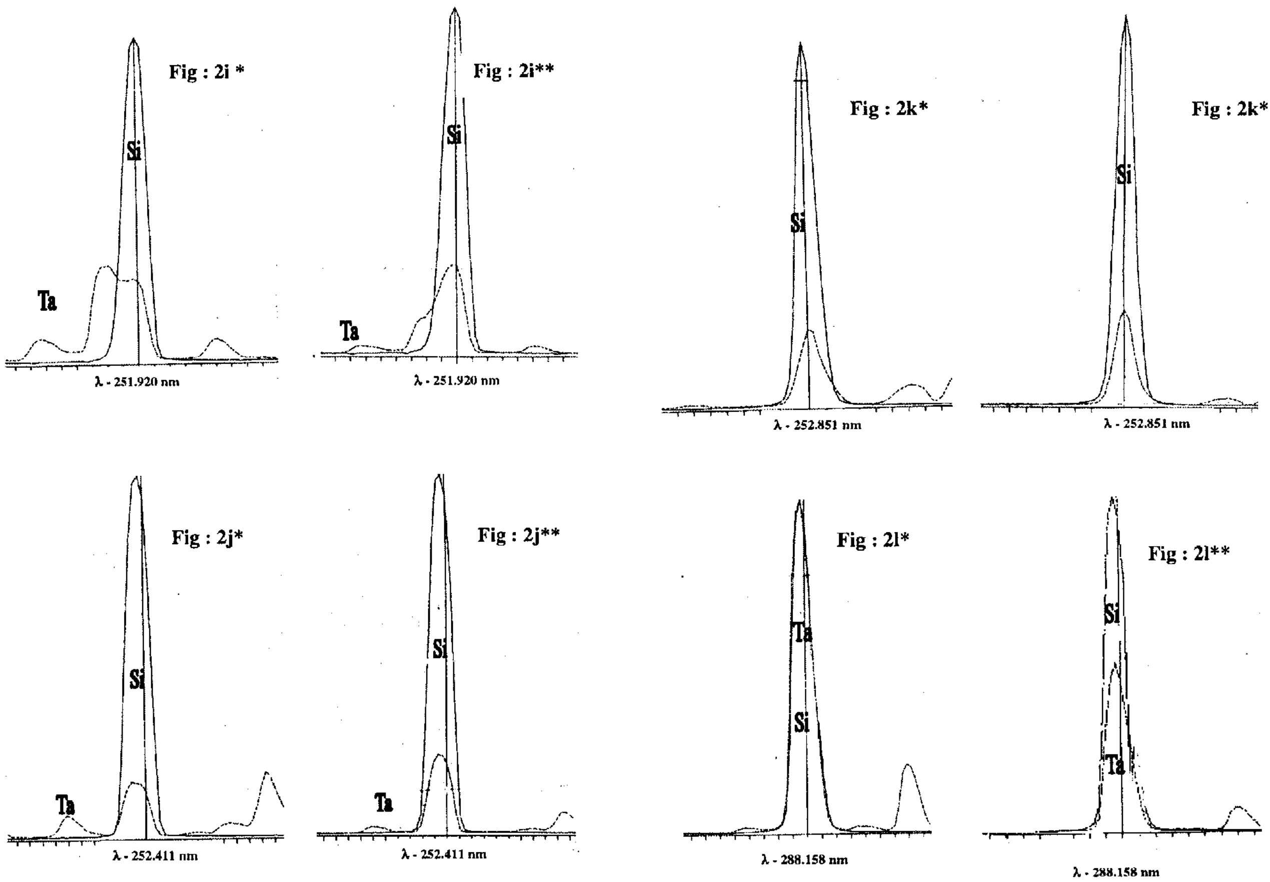

Fig. 2. Tantalum interference-free silicon line selection. *a)* Left wing overlap of Ta; *b)* right wing overlap of Ta; *c)* right and left wing overlap of Ta; *d)* left wing overlap of Ta; *e)* left wing overlap of Ta; *f)* right and left wing overlap of Ta; *g)* right and left wing overlap of Ta; *h)* no overlaps of Ta; *i)* left wing overlap of Ta; *j)* left wing overlap of Ta; *k)* no overlap of Ta; *l)* direct overlap of Ta.

10 mg cm^{-3} tantalum spectra (*) and with cupferron addition (**) overlapped over silicon 1 mg dm^{-3} spectra.

Partial precipitation reveals the decrease of tantalum peaks around and over silicon peak. Profiles of silicon were taken by overlapping the two of the above solutions individually, the depiction is shown in Fig. 2. It was observed that the lines at 251.611 nm and 252.851 nm showed no interference of tantalum in the vicinity of ± 0.02 nm, and the line at 288.158 nm had a direct tantalum overlap. The rest of the lines had either left or right wing overlap or both. In between 251.611 nm and 252.851 nm the highest sensitive line was chosen, *i.e.* at 251.611 nm.

During the dissolution of tantalum powder it was observed that the values of silicon found were less than the reported values (FTW-100 and STA-18KT). This was confirmed by dissolving tantalum powders in open vessel and closed vessel in clean room and the results are presented with a standard addition in Table 2. It was found that closed-vessel dissolution of tantalum pow-

Table 3. Direct Analysis of Tantalum Powder in Clean Room and Normal Laboratory* Using Closed Teflon Vessel

Sample	Direct analysis in clean lab			Direct analysis in normal lab		
	Analyzed values ρ /(mg dm^{-3})	1 mg dm^{-3}doped recovery/%	5 mg dm^{-3}doped recovery/%	Analyzed values ρ /(mg dm^{-3})	1 mg dm^{-3}doped recovery/%	5 mg dm^{-3}doped recovery/%
FTW-100	9.80 ± 0.11	98.25 ± 0.20	99.20 ± 0.26	13.22 ± 0.48	118.45 ± 0.32	109.53 ± 0.39
STA-18KT	2.83 ± 0.13	97.15 ± 0.23	99.20 ± 0.30	4.85 ± 0.36	109.67 ± 0.41	107.45 ± 0.36

Note: All results are average of five readings.
*± SD of 5 readings.

Table 4. Analysis of Silicon in Tantalum and its Compounds in Closed Vessel in Clean Room*

Sample	Direct analysis in clean room		
	Analyzed values ρ /(mg dm^{-3})	1 mg dm^{-3} doped recovery/%	5 mg dm^{-3} doped recovery/%
$Ta(OH)_5$	81.41 ± 1.23	97.45 ± 0.20	98.48 ± 0.18
K_2TaF_7	32.65 ± 0.85	98.51 ± 0.26	98.75 ± 0.17
Ta	19.23 ± 0.08	98.23 ± 0.24	98.88 ± 0.12

Note: All results are average of five readings.
*± SD of 5 readings.

der gave results very close to the reported values in comparison with open-vessel digestion because silicon gets volatilized as SiF_4. A slight increase in temperature was noted when the tantalum powder started dissolving in HF acid and HNO_3 mixture. This was not observed in the dissolution of $Ta(OH)_5$ and K_2TaF_7. Direct analysis of tantalum powders (FTW-100 and STA-18KT) was carried out in closed vessel with standard addition in clean room and in normal laboratory, the results are given in Table 3. It was observed that normal lab results showed an increase of silicon values, which was contributed by the environmental contamination. Analysis of $Ta(OH)_5$, K_2TaF_7 and sodium-reduced tantalum metal powder sample prepared is also given along with standard addition in Table 4. The present methodology of line selection developed for determination of trace silicon in tantalum and its related compounds is novel by using cupferron as line identification tool. The analysis of silicon in tantalum and its compounds was very accurate in comparison with certified powders. The selected silicon line at 251.611 nm is an interference-free line of tantalum for silicon and can be used for analysis of trace silicon in all tantalum-related matrices.

Acknowledgements. The authors would like to thank the Department of Information Technology (DIT), Govt. of India, New Delhi, for sponsoring tantalum technology mission project. They are also thankful to Dr. B. K. Das, Executive Director, Centre for Materials for Electronics Technology, Dr. K. S. K. Sai, Senior Director, and Dr. V. C. Sethi, Director, DIT, for their encouragement.

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