
**SELECTIVE DETERMINATION OF TANTALUM IN ORES
BY EXTRACTION WITH N-PHENYLBENZOHYDROXAMIC
ACID IN TOLUENE**

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Received October 13, 1989

Accepted December 22, 1989

A method for tantalum(V) spectrophotometric determination in a non-aqueous phase is proposed. Tantalum(V) is extracted with N-phenylbenzohydroxamic acid into toluene from a 5M hydrochloric acid solution. The colour is then developed by addition of 4-(2-pyridylazo)-resorcinol (PAR) solution in N,N-dimethylformamide and pyridine to an aliquot of the extracted phase. The Ta(V)-PAR complex gives an absorption maximum at 547 nm with a molar absorptivity of $3.88 \pm 0.04 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. The method has been applied to the selective determination of tantalum in ores with good accuracy and precision.

Owing to the lack of sensitivity and selectivity of most spectrophotometric reagents, solvent-extraction is frequently used as a prior separation step in trace metal analysis. Spectrophotometric determination after extraction is normally carried out in aqueous solution after re-extracting the complexed metal or mineralizing the extract. Also, direct measurement of the absorbance of the complexed metal in the extracted solution is often carried out, but in many cases the reagent blank has a high absorbance.

In this work, tantalum is determined after its extraction with N-phenylbenzohydroxamic acid (PBHA) in toluene. The spectrophotometric reaction is carried out directly in the toluene extract, without back extraction, by adding a solution of 4-(2-Pyridylazo)-resorcinol (PAR) in N,N-dimethylformamide (DMF) and pyridine to adjust acidity of the non-aqueous solution.

Direct complex formation in the non-aqueous extract by adding a suitable spectrophotometric reagent has been used previously for the determination of zinc, boron, uranium and niobium (refs¹⁻⁴).

In this work tantalum is determined in ores in the presence of large amounts of other metal ions. Interference of low levels of Nb can be eliminated with NaF as masking agent, and large amounts of interfering Fe(III) ions can also be eliminated by prior separation into IBMK.

EXPERIMENTAL

Apparatus and Reagents

A Pye Unicam SP8-100 automatic recording spectrophotometer with 1-cm silica cells was used. An Orion microprocessor based Ion-analyzer Model 901 with glass and saturated calomel electrodes was used for pH determinations.

All chemicals were of analytical reagent grade (Merck). Tantalum(V) stock solution, $1 \text{ mg} \cdot \text{ml}^{-1}$, was prepared from Ta(V) oxide by fusion with KHSO_4 in a Pt crucible and dilution with 4% ammonium oxalate solution. Ta(V) standard working solutions were prepared by diluting the stock solution with 4% ammonium oxalate immediately before use. A 1% PBHA solution in ethanol was prepared daily. A 0.15% PAR solution in DMF was used. Stock solutions of other ions (10^{-2} M) were prepared by dissolving appropriate amounts of suitable salts in $0.01 \text{ M} \text{ -HNO}_3$.

Procedure for Dissolution of Tantalum Ore

Weigh an appropriate amount of 200-mesh tantalum ore (0.05 to 0.15 g) in a platinum crucible. Add 2 g of potassium bisulphate and warm in a flame carefully (avoiding the sample splashing or spitting) for 10 min. Increase the crucible temperature to disperse the sample and maintain it for approximately 20 min. Leave to cool to room temperature and dissolve the solid with a warm solution ($70\text{--}90^\circ\text{C}$) of 4% ammonium oxalate solution. Then leave to cool and dilute to 100 ml with the same oxalate solution in a calibrated flask.

Extraction of Tantalum

Pipette 1 ml of an aliquot of the sample solution (containing up to $200 \mu\text{g}$ of tantalum) into a separating funnel. Add 8 ml of hydrochloric acid (1 : 1) (v/v), 1 ml of fluoride solution (5 g l^{-1}) and 1 ml of PBHA solution 1% in ethanol. Extract with 10 ml of toluene by mechanical shaking for 5 min and allow the phases to separate for 10 min. Filter the toluene extract through dry cotton-wool and discard the aqueous phase.

Spectrophotometric Determination of Tantalum

Pipette 2 ml of the extracted solution, 3 ml of the 0.15% PAR solution in DMF and 5 ml of pyridine into a calibrated flask. Heat at $50 \pm 3^\circ\text{C}$ for 10 min in a thermostatic bath, then cool and dilute if necessary with toluene up to 10 ml. Measure the absorbance at 547 nm against a reagent blank, prepared by the same procedure but not containing tantalum.

Prepare a calibration graph by taking independent aliquots of Ta(V) standard solutions, extracting them from 5M-HCl solutions and applying the above spectrophotometric procedure.

RESULTS

Tantalum(V) is quantitatively extracted with PBHA from an aqueous solution 5 to 9M HCl, with a molar ratio $\text{TaOCl}_2^{2+} : \text{PBHA} : \text{Cl}^-$ of 1 : 2 : 2 (ref.⁴). The extracted Ta-PBHA ion-association complex is coloured, which permits the spectrophotometric determination of Ta, but sensitivity is low (maximum molar absorptivity is less than $1.2 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$). Maximum sensitivity with PAR as spectrophoto-

metric reagent was achieved by extracting Ta–PBHA complex from a hydrochloric acid solution in a concentration range from 5 to 9 mol l⁻¹. The optimum PBHA concentration in ethanol (addition of 1 ml to the aqueous phase) was found to be 10 g l⁻¹.

In such conditions, niobium(V) is also extracted into the non-aqueous solvent with PBHA (ref.⁴). However, interference of this element was eliminated by adding NaF as masking agent, as indicated in Table I. In preliminary assays, several spectrophotometric reagents (triphenyl-methane derivatives) were tested for complexing the extracted tantalum–PBHA (as ion-association complexes). These reagents and results are summarized in Table II.

Procedure for tantalum determination involved addition to 3 ml of extract in toluene of 3 ml of 0.1% reagent solution in chloroform and diluting to 10 ml with toluene. In all cases, molar absorptivity coefficients were small, an excess of triphenyl-methane derivatives reagents (RH) was necessary and maximum absorptivity wavelength of Ta–RH complex and RH coincide. Addition of organic bases (pyridine, *t*-butylamine and 1-propylamine) did not improve the analytical performance. Better results with respect to selectivity, sensitivity and stability of absorbance were obtained with PAR as spectrophotometric reagent forming a chelate with Ta(V), as described in this paper. In this case, addition of an organic base (pyridine

TABLE I
Effect of foreign ions on the determination of 2.5 µg ml⁻¹ of tantalum(V)

Element	Tolerance limit ^a (µg per 50 µg of Ta(V))		Masking agent
	without masking agent	with masking agent	
Al, Mg, Co, Ca, Sr, Ba	10 000 ^b	—	—
Pb, Zn, Cu, Ni, Mn(II)	10 000 ^b	—	—
Fe(II)	5 000 ^b	—	—
Bi	5 000	—	—
F ⁻	2 500	—	—
VO ₃ ⁻	250	2 500	hydrazine sulphate, 5% solution
Fe(III)	2 500	10 000 ^b	previous extraction in MIBK + ascorbic acid, 10% solution
Nb(V)	25	500	NaF, 5% solution

^a The tolerance limits given are the concentration levels at which the interference causes an error in the tantalum determination of no more than 2.08%; ^b maximum amount tested.

produces the best performance) is necessary for complete development of colour and stability of absorbance.

From the organic bases *t*-butylamine, 1-propylamine and pyridine studied at several concentrations, addition of 5 ml of pyridine produced the best sensitivity and stability of absorbance. Owing to the slow reaction of Ta(V)-PBHA complex with PAR at room temperature, heating of the final solution was necessary. Heating the final solution at $50 \pm 3^\circ\text{C}$ for 10 min produced the maximum absorbance at 547 nm (molar absorptivity $3.4 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$). This absorbance remained stable for 30 min.

Concentration of PAR in DMF solution was also optimized. DMF was used for dissolving the spectrophotometric reagent due to its high dielectric constant. In addi-

TABLE II

Spectrophotometric reagents used for colour development in the toluene extract of Ta-BPHA complex

Reagent	$\epsilon_{\max} \cdot 10^{-4}$ $\text{l mol}^{-1} \text{ cm}^{-1}$	λ_{\max} nm
Brilliant green	2.62	635
Malachite green	2.50	625
Bromophenol blue	1.81	420
Dibromo- <i>o</i> -cresol-sulphophthalein	1.40	418
Thymol blue	3.70	553
Methyl red	2.40 ^a	488

^a Stability of absorbance was less than 15 min.

TABLE III

Results of the determination of Ta in ores by the described procedure

Sample	Ta expected, %	Ta found ^a , %	Relative error, %
IGS-34 ^b	40.88	41.71 \pm 0.86	2.03%
A ^c	10.65	10.85 \pm 0.22	1.87%
B ^c	2.43	2.40 \pm 0.06	-1.23%
C ^d	20.61	21.01 \pm 0.44	1.94%

^a Mean \pm r.s.d. of five determinations; ^b certified composition of tantalite ore (IGS-34) is: 40.88% Ta, 18.83% Nb and 0.69% Ti; ^c synthetic samples: IGS-34 + CaCO₃ (A. R. Merck);

^d synthetic sample: IGS-34 + Fe₂O₃ (A. R. Merck).

tion DMF favoured both the rupture of the ion-pair associate Ta–PBHA and formation of the chelate with PAR (ref.⁵). The Ta(V)–PAR complex in the non-aqueous media exhibits a maximum of absorbance at 547 nm when measured against a similar reagent blank, with a molar absorptivity of $3.88 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. It is noticeable that an increment in sensitivity is observed with respect to the PAR–Nb(V) complex in aqueous medium ($\epsilon \approx 1.7 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 535 nm). At 547 nm Beer's Law was obeyed at Ta(V) levels up to 40 μg ($4 \mu\text{g ml}^{-1}$) of Ta in the final measured solution. The relative standard deviation for eight determinations of $3.0 \mu\text{g ml}^{-1}$ of Ta(V) was 2.08%.

The effect of several elements most frequently associated with tantalum in ores was studied. The interference produced by large amounts of Fe(III) can be eliminated with prior extraction of this element with 20 ml of IBMK, which did not cause loss of Ta(V). Interference from any remaining Fe(III) is easily eliminated by reduction to Fe(II) with 5% solution of ascorbic acid.

Nb(V) causes a severe interference at a mass ratio of 1 : 1 to Ta(V). Attempts to mask Nb(III) with SCN^- (after reduction of Nb(V) with SnCl_2) did not improve selectivity in the determination of Ta(V) with respect to this element. However, the tolerance limit can be increased by masking Nb(V) with fluoride anion. Vanadium(V) also caused interference at a mass ratio of V : Ta = 5 : 1. Reduction to V(III) gave no interference at a mass ratio of 50 : 1. Hydrazine sulphate as reducing agent (5% solution) gave better results than oxalic or ascorbic acids.

The method was applied to the determination of tantalum in a natural ore and synthetic samples. A Tantalite ore (IGS-34) certified by the Institute of Geological Sciences (London) was used as the standard sample. The samples IGS-34, A and B (Table III) were analysed following the procedure described above, and sample C after elimination of Fe(III) with prior extraction into IBMK. The results obtained agreed well with the expected values, as illustrated in Table III.

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