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TAN-1: A CERTIFIED TANTALUM REFERENCE ORE

H.F. STEGER AND W.S. BOWMAN

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TAN-1: A CERTIFIED TANTALUM REFERENCE ORE/ TAN-1: MINERAI DE RÉFERÉNCE DE TANTALE

by/par

H.F. Steger* and/et W.S. Bowman**

SYNOPSIS

A 232-kg sample of a tantalum ore TAN-1 from Bernic Lake, Manitoba, was prepared as a compositional reference material. TAN-1 was ground to minus 74 µm, blended in one lot and bottled in 200-g units. Its homogeneity was confirmed by an X-ray fluorescence technique for tantalum.

In a "free choice" analytical program, 19 laboratories contributed results for tantalum in one bottle of TAN-1. Based on a statistical analysis of the data, a recommended value was assigned for Ta at 0.236%.

Un échantillon de 232 kg d'un minerai de tantale, provenant de Bernic Lake en Manitoba, a été préparé comme matériau de référence de composition. Le TAN-1 a été broyé à une granulométrie de moins 74 µm, mélangé en lot de minerai et embouteillé en unités de 200 g. L' homogénéité de TAN-1 a été confirmée pour le tantale par une méthode analytique utilisant la fluorescence X.

En vertu d'un programme analytique de "libre-choix", 19 laboratoires ont fourni des résultats sur un flacon de TAN-1 pour le tantale. L'analyse statistique des données a été utilisée pour assigner une valeur recommandée de 0,236% pour le tantale.

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Note: Major contributions were also made by other staff members of the Mineral Sciences Laboratories./ Avec la collaboration de d'autres membres du personnel des Laboratoires des sciences minérales.

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INTRODUCTION

The preparation, characterization and certification of the tantalum ore TAN-1 is another facet of the continuing endeavour of the Canadian Certified Reference Materials Project (CCRMP) to provide compositional reference ores, concentrates and related products typical of Canadian deposits and not, in general, available from other sources for use in analytical laboratories associated with mining, metallurgy and the earth sciences. Other reference materials certified by CCRMP are described in a catalogue available from CANMET, Energy, Mines and Resources Canada, Ottawa (1).

TAN-1 was chosen to serve as a reference material for use in the analytical laboratories associated with the tantalum mining industry. An interlaboratory program was conducted to obtain results for tantalum from 19 laboratories using analytical methods of their choice. The results should therefore be representative of the current state of the analysis for tantalum in commercial, industrial and government establishments.

NATURE AND PREPARATION OF TAN-1

The raw materials for TAN-1 were donated to CCRMP in November 1974 by the Tantalum Mining Corporation of Canada Limited and consisted of 308 kg of ore typical of the deposit at Bernic Lake, Manitoba, and 1 kg of tantalite concentrate prepared from the ore.

The orebody consists of a gently dipping tabular body of complex pegmatite of irregular zones each having a distinctive mineral assemblage (2). The tantalum minerals consist of wodgenite, $(Ta, Nb, Sn_{2x})_2 (Mn, Fe, Sn_x)O_6$, and lesser amounts of microlite, $(Ca, Na)_2 (Ta, Nb)_2 O_6 (OH, F, O)$, and occur in two such assemblages; these are a coarse partially sericitized perthitic microcline and a relatively unaltered, fine-grained bluish-white aplitic albite. The wodgenite is present as disseminated grains varying from less than 1 to 10 mm in diameter.

In March 1981, the ore and concentrate were dry-ground to pass a 74 μm screen in separate preparations. Two hundred and thirty-two kilograms of the powdered ore and the 1 kg of concentrate were tumbled in a 570-L conical blender for 18 h and bottled in 200 g units.

The analysis of 30 randomly-selected bottles of TAN-1 by X-ray fluorescence demonstrated the material to be sufficiently homogeneous for use as a reference material. The results of the confirmation of the homogeneity of TAN-1 are reported in Appendix A.

The approximate chemical composition and particle size analysis are given in Tables 1 and 2.

Table 1 - Approximate chemical composition of TAN-1

Element	wt %*
Si	33.40
Al	8.16
Na	4.49
K	1.47
Ca	0.46
Ta	0.236
Fe	0.17
Sn	0.07
Mg	0.02
Mn	0.02
Nb	0.02

* - Mean of a minimum of two determinations or certified value

Table 2 - Particle size analysis (wet screen)

Size of fraction (μm)	wt %*
-104 + 74	0.02
-74 + 55	0.3
-55 + 46	19.9
-46 +37	12.2
-37	67.6

* - Mean of duplicate determinations

INTERLABORATORY PROGRAM FOR CERTIFICATION

The laboratories that participated in the certification program are listed in Appendix B. Each was assigned a code number which bears no relation to its alphabetical order. The results from CANMET are reported as Laboratory 2.

Each laboratory was requested to contribute five replicate results for tantalum for one bottle of TAN-1 using the method of its choice and to report results on an "as is" basis. When a laboratory submitted results by more than one method or performed different sets of analysis on different days each set was considered to be statistically independent.

The recommended value for tantalum is presented in Table 3. Methodological and analytical information is presented in Tables 4 and 5. Values of niobium from two laboratories are given in Table 6.

Table 3 - Recommended value and associated statistical parameters for tantalum in TAN-1

No. of laboratories		18
No. of results		126
Mean		0.236%
95% confidence limits		
	low	0.232%
	high	0.241%
σ_A	0.007%	

Table 4 - Summary of analytical procedures

Method	Laboratory No.	Decomposition/Separation	% Ta
X-ray fluorescence	1	$Na_2B_4O_7$ + WO_3 fusion; calibration curve	0.211
	3	$Li_2B_4O_7$ + La_2O_3 fusion; calibration curve	0.249
	4	$Li_2B_4O_7$ fusion; standard addition	0.242
	5(a)	Briquette using sodium alkylaryl sulfonate binder; calibration curve	0.258
	5(b)	$Na_2B_4O_7$ + WO_3 fusion; calibration curve	0.249
	6	$Li_2B_4O_7$ fusion; calibration curve	0.237
	7(a)	Fusion with $Na_2B_4O_7$ + SiO_2 + NaF; calibration curve	0.232
	7(b)	$Na_2B_4O_7$ fusion; standard addition	0.247
	13	Not defined; standard addition	0.163
	14	$Li_2B_4O_7$ + CaF_2 fusion; calibration curve	0.229
	18	Fusion with "Spectroflux 100"; calibration curve	0.249
DCP - optical emission	8	Fusion with Na_2O_2; leaching with HCl + HF; Ta extracted into and measured in MIBK phase	0.235
	10	Fusion with $LiBO_2$; leaching with HCl + HF to dryness; Ta into and measured in 10% HCl - 2% HF	0.238
	12	Fusion with NaOH + Na_2O_2; taken up in HCL + H_2SO_4 + HF	0.218
	17	Fusion with $LiBO_2$; taken up in HNO_3 + HF	0.242

Table 4 - Continued

Method	Laboratory No.	Decomposition/Separation	% Ta
ICP - atomic emission	13	HF + HNO_3	0.212
	14	HCl + HF to dryness; fused with Na_2O_2 + Na_2CO_3; taken up in 50% HCl containing scandium	0.241
	19	Fusion with $LiBO_2$	0.237
Neutron activation analysis	9	Instrumental thermal neutron activation analysis	0.236
	13	Ta-182 γ-spectra was measured 5 days after irradiation	0.235
	15	Ta-182 1.12 MeV peak was measured 6 days after irradiation	0.224
Colorimetry	2	Fusion with Na_2CO_2; taken up in H_2SO_4 + HF; Ta extracted MIBK and stripped with 1.5% hydrogen peroxide and taken to dryness; taken up in HF - oxalic acid and measured as hexafluoride - brilliant green ion association complex after its extraction into benzene	0.246
	15	HF + H_2SO_4; residue fused with $NaHSO_4$; dissolved in tar- and treated with H_2S; precipitate filtered off and Ta determined in the filtrate by pyrogallol method	0.221
Atomic absorption	11	Fused with KOH; taken up in HNO_3 + HF + H_2SO_4; Ta extracted into and measured in MIBK containing 5% aliquot 336.	0.245
Gravimetry	8	HF + HNO_3 to dryness; residue treated with HCl + HF; passed through Dowex ion-exchange resin; Ta eluate was treated with H_3BO_3; HCl and cooled to 10°C; Ta precipitated with Cupferron and ignited to the oxide.	0.234

Table 5 - Analytical results, laboratory means, and standard deviations for TAN-1

Tantalum, Wt %

						Mean	S.D.
Lab- 1 (XRF)	0.213	0.213	0.205	0.213	0.213	.2114	.0036
Lab- 2 (COLOR)	0.242	0.248	0.250	0.248	0.241	.2458	.0040
Lab- 3 (XRF)	0.256	0.259	0.236	0.247	0.248	.2492	.0090
Lab- 4 (XRF)	0.24	0.24	0.24	0.25	0.24	.2420	.0045
Lab- 5 (XRF)	0.264	0.260	0.260	0.245	0.263	.2584	.0077
Lab- 5 (XRF)	0.247	0.247	0.251	0.256	0.245	.2492	.0044
Lab- 6 (XRF)	0.238	0.236	0.234	0.234	0.241	.2366	.0030
Lab- 7 (XRF)	0.214	0.205	0.262	0.241	0.239	.2322	.0228
Lab- 7 (XRF)	0.198	0.280	0.262	0.255	0.238	.2466	.0311
Lab- 8 (DCP)	0.254	0.229	0.223			.2353	.0164
Lab- 8 (GRAV)	0.221	0.251	0.231			.2343	.0153
Lab- 9 (NAA)	0.2398	0.2361	0.2358	0.2352	0.2332	.2360	.0024
Lab- 10 (DCP)	0.238	0.236	0.238	0.241	0.237	.2380	.0019
Lab- 10 (DCP)	0.236	0.240	0.237	0.237	0.236	.2372	.0016
Lab- 10 (DCP)	0.240	0.238	0.240	0.239	0.238	.2390	.0010
Lab- 11 (AA)	0.246	0.249	0.241	0.240	0.247	.2446	.0039
Lab- 12 (DCP)	0.22	0.22	0.22	0.22	0.21	.2180	.0045
Lab- 13 (NAA)	0.221	0.240	0.227	0.238	0.249	.2350	.0111
Lab- 13 (ICP)	0.219	0.220	0.210	0.212	0.201	.2124	.0077
*Lab- 13 (XRF)	0.1597	0.1614	0.1666			.1626	.0036
Lab- 14 (XRF)	0.228	0.230	0.227	0.230	0.229	.2288	.0013
Lab- 14 (ICP)	0.240	0.239	0.243	0.238	0.243	.2406	.0023
Lab- 15 (NAA)	0.2266	0.2204	0.2302	0.2230	0.2183	.2237	.0048
Lab- 15 (COLOR)	0.2232	0.2237	0.2234	0.2224	0.2129	.2211	.0046
*Lab- 16 (DCP)	0.165	0.152	0.162	0.155	0.152	.1572	.0060
Lab- 17 (DCP)	0.26	0.25	0.24	0.23	0.23	.2420	.0130
Lab- 18 (XRF)	0.254	0.246	0.249	0.250	0.246	.2490	.0033
Lab- 19 (ICP)	0.2395	0.2335	0.2335	0.2360	0.2425	.2370	.0039

*Outliers

Table 6 - Reported values for niobium in TAN-1

Laboratory	Method	No. of Results	Mean %
2	X-ray fluorescence	1	0.010
14	X-ray fluorescence	5	0.020
	ICP - AE	5	0.022

DETECTION OF OUTLIERS

Two sets of results whose means differed by more than twice the overall standard deviation from the initially calculated mean value were not used in subsequent computations to avoid biasing of the statistics. All results that were rejected are identified in Table 5.

ESTIMATION OF CONSENSUS VALUE AND 95% CONFIDENCE LIMITS

A one-way analysis of variance technique was used to estimate the consensus value and variance. This approach considers the results of the described certification program to be only one sampling out of a universal set of results. The analytical data were assumed to fit the model (3).

$$x_{ij} = \mu + y_i + e_{ij}$$

where x_{ij} = the j^{th} result in set i,
μ = the true consensus value,
y_i = the descrepancy between the mean of the results in the set i ($\bar{x}_i.$) and μ, and
e_{ij} = the discrepancy between x_{ij} and $\bar{x}_i.$

It is assumed that both y_i and e_{ij} are normally distributed with means of zero and variances of ω^2 and σ^2, respectively. The significance of ω_2 is detected by comparing the ratio of between-set mean squares to within-set mean squares with the F statistic at the 95% confidence level and with the appropriate degrees of freedom.

The consensus value of the assumed model is estimated by the overall mean $\bar{x}..$ by:

$$\bar{x}.. = \sum_i^k \sum_j^{n_i} x_{ij} \Big/ \sum_i^k n_i$$

where n_i = the number of results in set i, and
k = the number of sets.

The value of σ^2 is esimated by s_1^2 which is given by

$$s_1^2 = \sum_i^k \sum_j^{n_i} (x_{ij} - \bar{x}_i.)^2 \Big/ \sum_i^k n_i - k$$

The value of ω^2 is estimated by

$$\omega^2 = (s_2^2 - s_1^2) \Big/ \frac{1}{k-1} \left(\sum_i^k n_i - \sum_i^k n_i^2 \sum_i^k n_i \right)$$

where

$$s_2^2 = \sum_i^k n_i (\bar{x}_i. - \bar{x}..)^2 \Big/ k-1.$$

The variance of the overall mean is given by

$$V[\bar{x}..] = \left(\sum_i^k n_i^2 / (\sum_i^k n_i)^2 \right) \omega^2 + \left(1/\sum_i^k n_i \quad \sigma^2 \right)$$

and the 95% confidence limits for $\bar{x}..$ are

$$\bar{x}.. \pm t_{0.975,\,(k-1)} \sqrt{V[\bar{x}..]}$$

It should be noted that 95% confidence limits denote that if the certification program were performed 100 times, the overall mean would fall within the prescribed limits in 95 instances.

The average within-set standard deviation, σ_A, is a measure of the average within-bottle precision as determined by the analytical methods used. The implication exists therefore that a laboratory using a method of average or better reproducibility should obtain individual results for a given certified element with a precision that is at least comparable to the reported value of σ_A.

CRITERION FOR CERTIFICATION

The ratio of the between-laboratory-mean to the within-laboratory standard deviation, σ_B/σ_A, where

$$\sigma_B = \sqrt{\sum_i^k (\bar{x}_i. - \bar{x}..)^2 \Big/ (k-1)}$$

is a measure of the quality of the certification data for the reference materials of CCRMP (4). The acceptable upper limit for σ_B/σ_A is 3 for all elements except uranium for which an upper limit of 2 is more realistic.

The criterion for the certification of an element in a reference material is RP, the percentage of sets of results that must be rejected to give a value of σ_B/σ_A equal to or less than the acceptable upper limit. RP should not exceed 15%. For TAN-1, RP equals 3.6%.

DISCUSSION

Table 4 is a summary of a methodological classification of the analytical results where there is a clear distinction between types of decomposition, separation, and determination steps. No attempt was made to detect a statistically significant difference between the overall means of the more popular methods.

Figure 1 depicts the histogram of the analytical data and illustrates clearly that there is very good consensus in the value for tantalum. It may be concluded therefore that the determination of this element, at least in the presence of only minor niobium, presents no great difficulty.

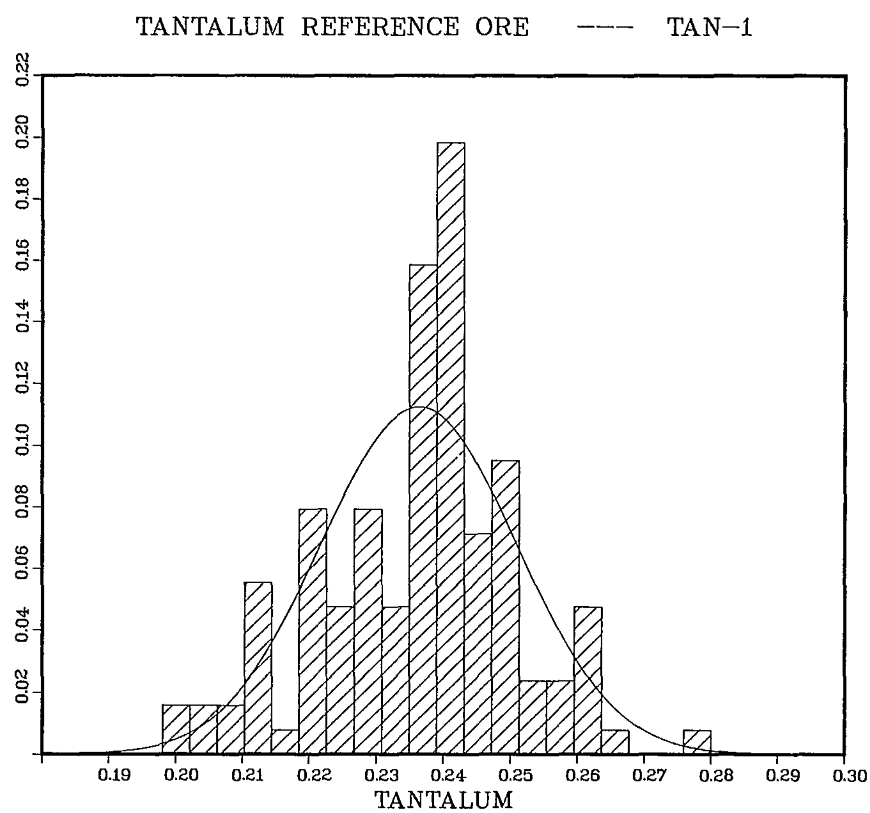

Fig. 1 - Histogram for tantalum

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APPENDIX A

CONFIRMATION OF HOMOGENEITY

CONFIRMATION OF HOMOGENEITY

The homogeneity of TAN-1 was confirmed by X-ray Assay Laboratories Limited by analyzing in quintuplicate 30 bottles by X-ray fluorescence. Since the stock of 1003 bottles could not be divided into 30 equal lots of 33 bottles, the following procedure was used. The code number of the first bottle was selected at random from bottles 1 to 33. The code numbers of the majority of the remaining bottles were given by the code number of the preceding bottle plus 33. The code numbers of Bottles 4, 10, 13, etc., were given by the code numbers of bottles 3, 9, 16, etc., plus 34. The results are shown in Table 7.

Table 7 - Confirmation of homogeneity of TAN-1 for tantalum

Bottle No.	Ta (No. of counts) Individual					Mean
15	1721.7	1719.0	1684.0	1698.7	1691.7	1703.0
48	1701.7	1690.3	1683.7	1694.7	1684.0	1690.9
82	1708.0	1681.3	1689.0	1676.0	1667.3	1684.3
115	1733.7	1702.0	1718.3	1715.3	1723.0	1718.5
148	1715.3	1739.3	1723.7	1745.0	1702.7	1725.2
182	1672.7	1692.7	1685.0	1695.7	1675.0	1684.2
215	1694.0	1695.7	1693.7	1693.7	1701.0	1695.6
248	1709.3	1711.0	1726.7	1695.7	1701.3	1708.8
282	1698.3	1713.0	1695.3	1697.0	1692.0	1699.1
315	1718.0	1683.3	1697.0	1688.0	1692.3	1695.7
348	1688.3	1692.0	1705.3	1686.0	1690.7	1692.5
382	1687.0	1670.0	1678.0	1687.0	1705.3	1685.5
415	1681.3	1679.0	1707.0	1686.7	1685.3	1687.9
448	1692.3	1678.0	1719.3	1692.0	1701.3	1696.6
482	1696.0	1705.3	1694.3	1704.0	1687.7	1697.5
515	1680.3	1722.3	1706.3	1694.3	1688.3	1698.3
548	1723.7	1683.0	1692.7	1692.0	1712.3	1700.7
582	1692.0	1704.3	1683.0	1691.7	1685.0	1691.2
615	1711.7	1695.7	1691.0	1674.3	1673.0	1689.1
648	1675.3	1696.0	1697.3	1677.7	1672.0	1683.7
682	1702.7	1705.3	1711.0	1697.3	1702.3	1703.7
715	1696.7	1690.0	1705.7	1715.7	1686.0	1698.8
748	1684.0	1662.3	1695.0	1696.7	1680.3	1683.7
782	1671.0	1690.0	1706.3	1679.0	1700.7	1689.4
815	1665.3	1687.0	1657.0	1666.3	1662.0	1667.5
848	1684.3	1672.7	1681.7	1682.7	1660.0	1676.3
882	1667.7	1694.0	1675.3	1671.0	1683.7	1678.3
915	1701.7	1694.7	1691.7	1688.7	1695.7	1694.5
948	1669.7	1667.7	1692.7	1699.7	1662.3	1678.4
982	1672.7	1677.0	1700.7	1675.0	1703.0	1685.7
					Overall mean =	1693.2

A one-way analysis of variance technique was used to assess the homogeneity (3). Herein, the ratio of the between-bottle to within-bottle mean square is compared with the F statistic at the 95% level of probability. Some statistical evidence of bottle-to-bottle inhomogeneity was found for tantalum.

Analysis of variance table for tantalum

Source of variation	Degrees of freedom	Mean square
Between bottles	29	7.264×10^2
Within bottles	120	1.537×10^2
Total		
Calculated F statistic =	4.725	
F.95(29,120) =	1.562	

Null hypothesis of no difference between bottles is rejected for tantalum

The above results indicate that TAN-1 has statistically significant inhomogeneity with respect to tantalum. This does not necessarily imply that the inhomogeneity is also physically significant; experimental difficulties could give rise to erroneous results. Moreover a detectable inhomogeneity, statistical, physical or both, does not necessarily disqualify a candidate reference material from its intended use provided its magnitude is acceptable in comparison with the overall uncertainty in the certified value for the element of interest. The between-bottle standard deviation for TAN-1 was calculated to be 10.7 counts for an overall mean of 1693.2 counts. The detected inhomogeneity therefore gives rise to a relative uncertainty of 0.63%, a value which CCRMP concluded would be acceptable in comparison with the overall relative uncertainty expected from the results of the interlaboratory program. This latter can be calculated to be 0.0108% Ta for the recommended value of 0.236% Ta, i.e., the overall relative uncertainty is 4.6%, thereby demonstrating TAN-1 to be sufficiently homogeneous for use as a reference material for tantalum.

The usual practice of CCRMP is to analyze only 15 bottles in triplicate to confirm the homogeneity of a reference material. Had this been done for TAN-1 only the first three results for bottles 15, 82, 148, etc., would have been available. Interestingly, the analysis of variance table for these 45 results is given below and indicates TAN-1 to be homogeneous with respect to tantalum, again suggesting TAN-1 to be acceptable for use as a reference material.

Analysis of variance table

Source of variation	Degrees of freedom	Mean square
Between bottles	14	362.52
Within bottles	30	182.53
Total	44	
Calculated F statistic =	1.986	
F.95(14,30) =	2.037	

Null hypothesis of no difference between bottles is accepted for tantalum

APPENDIX B

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PARTICIPATING LABORATORIES

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