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CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES

MINES BRANCH

MINES BRANCH INVESTIGATION REPORT

IR 70-63

November 6, 1970

THE DETERMINATION OF NIOBIUM IN LEAD-
ZIRCONIUM-TITANIUM PRECIPITATES,
CALCINED PRODUCTS, AND SOLUTIONS

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Extraction Metallurgy Division

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SYNOPSIS

A procedure is described for the determination of small amounts of niobium in lead-zirconium-titanium precipitates, calcined products, and solutions. Niobium is determined by spectrophotometric measurement, in the ether extract, of a colored complex formed by niobium and thiocyanate in the presence of stannous chloride. The effect of the sample matrix on niobium results was determined from blank measurements and by using standard addition techniques.

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INTRODUCTION

As part of a joint program carried out by the Mines Branch and the Defense Research Board to develop a chemical process for producing electronic ceramics, small amounts of various additives were added to the main lead-zirconium-titanium compound. Because varying the quantities of these additives has a considerable effect on the properties of the ceramics, close control of the amounts of the elements added is essential.

Accordingly, development work has been carried out in this laboratory on procedures for such additions. The development of procedures for iron and chromium has been described in EMT 66-4. The present report describes the work carried out on a method for the determination of niobium in similar sample material and describes a procedure applicable for niobium determination on the type of sample material being analyzed by the Almax Ceramics Ltd., Lindsay, Ontario*. A requirement of the procedure was that it be applicable in the microgram range for niobium that was present in the ratios of approximately 100 to 1 lead to niobium, 50 to 1 zirconium to niobium, and 1 to 1 titanium to niobium.

* In response to a request from H. Mercer, Chemist, Almax Ceramics Ltd.

Of the methods available for determining niobium in the presence of contaminants in large amounts, a colorimetric thiocyanate procedure was considered to be the most applicable^(1,2,3,4). Such a procedure has been used here for some time on other types of sample material and it was applied to these ceramic samples with and without preliminary sample treatment and separation of contaminants. Standard addition tests were used to validate the procedures and an evaluation was made of the effect of the sample matrix on results. Although ether has been used in this laboratory as the organic extractant, the less-volatile ethyl acetate has been used successfully by Grimaldi⁽³⁾ as a substitute for ether. He found that lead, zirconium and titanium had little or no effect on the colorimetric procedure at ratios of contaminant to niobium higher than would be encountered in the ceramic materials to be analyzed here. It seemed reasonable, therefore, to expect that ether extraction would prove equally suitable for use in the presence of these three elements.

APPARATUS AND REAGENTS

Apparatus

Beckman Model B Spectrophotometer (or suitable alternative instrument).

Funnels, Separatory: 60 ml in size.

Reagents

Standard Niobium Solution

Fuse 100 mg of niobium oxide (Nb_2O_5) or the equivalent, with 4 grams of fused sodium pyrosulphate (finely ground) in a platinum, silica or quartz vessel. After cooling, dissolve the melt in 1 M tartaric acid and dilute to the mark in a 500-ml volumetric flask with 1 M tartaric acid(a).

Ammonium Thiocyanate Solution

Dissolve 20 grams in 100 ml water. Prepare fresh daily.

Stannous Chloride Solution

Ten grams of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in 15 ml of concentrated hydrochloric acid and diluted to 100 ml. Prepare fresh every second day.

Sodium Pyrosulphate

Reagent grade, fused.

Tartaric Acid, 0.5 M Solution

75.5 grams of reagent-grade tartaric acid per litre.

Hydrochloric Acid-Tartaric Acid Solution

15 grams of tartaric acid dissolved in 100 ml of 9 M hydrochloric acid.

Ethyl Ether, Peroxide Free

Shake the ether with 1/10 its volume of 10% stannous chloride solution on the day it is to be used.

(a) Solutions containing niobium must be at least 0.5 M in tartaric acid in order to prevent hydrolysis of the niobium.

PROCEDURE

Dissolution of Non-Refractory Sample Material

Weigh 0.25 to 1.0 g of sample into a beaker, add 10 ml of concentrated nitric acid first and then 5 to 10 ml of concentrated perchloric acid. Take to heavy fumes. Cool, add 5 ml of sulphuric acid, and take to sulphuric fumes. Cool; take up the salts with a 0.5 M tartaric acid solution, adding 1-2 ml of concentrated hydrochloric acid if necessary to obtain complete solution. Make the solution up to volume in a volumetric flask with 0.5 M tartaric acid solution.

Dissolution of Refractory Sample Material

Weigh out 0.25 to 1.0 g of sample into a 100-ml platinum dish. Add 10 ml of concentrated nitric acid, 20 ml of concentrated hydrofluoric acid, 5 ml of concentrated perchloric acid, and 3 ml of concentrated sulphuric acid; digest the sample on a hot plate at medium heat until nearly dry. Add 5 drops of concentrated sulphuric acid, heat just to fumes, cool, and add 5 g (weighed) of potassium pyrosulphate. Fuse over a Meker burner until the melt is clear and no sample residue is left undissolved. Cool. Add 5 drops of concentrated sulphuric acid and reheat until the melt is just clear. Cool; leach the melt with 0.5 M tartaric acid solution, adding 1-2 ml of concentrated hydrochloric acid to aid in solution of the melt. Transfer the clear solution to

an appropriate volumetric flask. Make any further dilutions for the colorimetric finish in 0.5 M tartaric acid^(b).

Color Development

Transfer an aliquot (1 to 5 ml) of the solution to a 60-ml separatory funnel and adjust the volume if necessary to 5 ml. Add 5 ml of HCl-tartaric acid solution reagent by pipette, then 5 ml of ammonium thiocyanate reagent by burette, followed immediately by 5 ml of peroxide-free ether added by pipette. Without delay, shake the funnel for 30 seconds (timed). After the layers have completely separated, drain off and discard the lower aqueous phase. Add 2 ml of stannous chloride solution to the ether fraction. Shake the mixture for 10 seconds, allow the phases to separate and drain off and discard the lower phase. Repeat the treatment of the ether layer with stannous chloride, if necessary^(c). Transfer the ether phase to a 10-ml volumetric

(b) The amount of tartaric acid present has an effect on the color intensity of the niobium-thiocyanate complex. Therefore, it is necessary to have the same amount of tartaric acid in each separatory funnel, for samples, standards and the blank. This becomes important if, for example, it is found that too small an aliquot has been taken for the final dilution, and the optical density is too low for accurate reading. To take a larger aliquot will necessitate the use of similar aliquots of the standard and blank solutions. For this reason, use of a more concentrated final solution volume is preferred to taking a larger final aliquot.

(c) The stannous chloride wash is repeated until the color intensity appears to be constant. All extracts should be washed with stannous chloride the same number of times.

flask, add acetone to the mark, and mix. Carry a reagent blank and standards covering the range 1 to 30 micrograms of Nb_2O_5 , along with the sample. Preferably, prepare the standards in a matrix similar to that present in the samples being analyzed*, or apply a correction factor based on analyzed synthetic samples or standard addition tests to typical sample material. Determine the optical density of the yellow-colored extract at a wavelength of 385 millimicrons on the Beckman "B" spectrophotometer using 1-cm Corex cells and a filter.

EXPERIMENTAL

Preliminary Observations

In preliminary work on this sample material, solution and solid samples were subjected to treatment with 1) nitric and perchloric acids, 2) nitric, perchloric, and sulphuric acids, and 3) pyrosulphate fusion, following acid treatment. These tests showed that the method of treatment had a considerable effect on niobium results. Also, it was indicated that the absorbance reading resulting from blanks carried through the procedure varied considerably with the type of sample treatment.

Unfortunately, certified standard samples or other analyzed samples representing this type of sample material were not available for the purpose of testing the procedure. Therefore, several prepared synthetic samples were made up for this purpose.

*for example, using a niobium-free product or synthetic mixture of similar composition as a base

TABLE 1

Sample Composition of Typical Ceramic Sample
Materials Submitted for Analysis

Sample No. EMM- and Sample Description	Lead Present g/l or % Pb	Zirconium Present g/l or % Zr	Titanium Present g/l or % Ti	Nitrate Present g/l or % NO ₃	Niobium Present g/l or % Nb ₂ O ₅	H ₂ O Present- Loss at 105°C %
X - Niobium-Free Solution Sample	30	12	0.3	-	-	-
373-Precipitation Feed Solution	29.6	12.1	0.33	160.	0.25	-
384-Precipitation Feed Solution	28.3	11.5	0.32	155.	0.50	-
517-Precipitation Feed Solution	27.3	11.0	0.31	154.	0.75	-
967-PZT 95-N-1 Ceramic	53.6	22.3	0.64	5.2	-	3.6
968-PZT 95-N-2 Ceramic	54.6	22.2	0.63	4.1	0.5	4.0
969-PZT 95-N-3 Ceramic	55.1	22.2	0.64	1.9	1.0	4.6
970-PZT 95-N-4	54.6	21.4	0.64	3.3	1.5	4.6
1693-PZT 95-N-5 Spray Dried at 700°C	59.7	23.9	0.68	-	1.0-1.5	0.27
1694-PZT 95-N-6 Organic Treatment - Dried at 700°C	59.5	23.8	0.68	-	1.0-1.5	0.17

A series of tests was then carried out (a) to establish the blank effect caused by the sample treatment and the sample composition, (b) to determine the niobium recovery obtained on prepared synthetic samples, (c) to run standard addition tests on actual sample material, (d) to separate niobium from contaminants using solvent extraction systems of methyl isobutyl ketone 1) with hydrofluoric and sulphuric acids, and 2) with hydrofluoric and nitric acids, and (e) to compare results on actual samples using different treatments.

(a) Matrix Blank Effect

The blank effects contributed by the dissolution procedure and by the constituents, lead, zirconium, and titanium, alone and in combination, in the amounts found in a typical sample, are shown in Table 2. Because a mixed acid attack followed by a pyrosulphate fusion was the most generally applicable treatment for all the sample material tried, it was chosen as representative of a typical blank.

(b) Niobium Recovery from Prepared Synthetic Samples

Measured amounts of niobium were added to carefully prepared synthetic samples representing typical sample compositions, and the niobium was then determined by comparison with a prepared sample matrix containing no niobium. These results and the effect of various blank corrections on niobium recovery are shown in Table 3.

TABLE 2

Blank Effect of Potassium Pyrosulphate,
Titanium, Zirconium, and Lead

Type of Blank	Absorbance		% Effect of Blank in Terms of an Average Sample Absorbance of 0.300	
	Gross	Net	Gross	Net
Reagent	.012	.012	4	4
Reagent + Potassium Pyrosulphate ($K_2S_2O_7$)	.026	.014 a	9	5
Reagent + $K_2S_2O_7$ + 16 μ g Ti	.036	.010 b	12	3
Reagent + $K_2S_2O_7$ + 607 μ g Zr	.044	.018 b	15	6
Reagent + $K_2S_2O_7$ + 1482 μ g Pb	.049	.023 b	16	8
Reagent + $K_2S_2O_7$ + 4 μ g Ti + 152 μ g Zr + 370 μ g Pb	.030	.014 b	10	5
Reagent + $K_2S_2O_7$ + 8 μ g Ti + 304 μ g Zr + 740 μ g Pb	.047	.028 b	16	9
Reagent + $K_2S_2O_7$ + 16 μ g Ti + 607 μ g Zr + 1480 μ g Pb	.065	.039 b	22	13

a - less reagent blank

b - less reagent + appropriate $K_2S_2O_7$ blank (approximately
30 mg $K_2S_2O_7$ per 1-ml sample aliquot taken)

TABLE 3

Effect of the Sample Matrix on Niobium Determination

Composition of Synthetic Sample			Niobium Added μg Nb_2O_5	Niobium Recovered ^a μg Nb_2O_5		
μg Ti	μg Zr	μg Pb		After Deducting Reagent Blank	After Deducting $\text{K}_2\text{S}_2\text{O}_7$ Blank	After Deducting Matrix Blank
12	-	-	9.0	9.70	9.27	9.07
16	-	-	12.0	12.85	12.3	12.0
-	455	-	9.0	9.70	9.27	8.94
-	607	-	12.0	12.3	11.7	11.1
-	-	1112	9.0	9.93	9.50	9.17
-	-	1482	12.0	12.7	12.1	11.36
4	152	371	3.0	3.21	3.11	2.89
8	304	742	6.0	6.30	6.03	5.75
12	455	1112	9.0	9.38	9.14	8.20
16	607	1482	12.0	12.9	12.35	11.1

a - large aliquot evaporated to fumes of sulphuric acid, then taken to dryness and fused with $\text{K}_2\text{S}_2\text{O}_7$

(c) Standard Addition Tests on Typical Sample Material

Standard addition tests were run on typical solution and solid sample materials using several sample preparation procedures. These results are shown in Table 4.

(d) Separation of Niobium from Contaminants using Solvent Extraction

The separation of niobium from most other elements by extraction with a ketone, such as methyl isobutyl ketone (MIBK), using a hydrofluoric acid solution in conjunction with a mineral acid(5,6,8,9), was attempted. Acid mixtures of 7 M HF-5 M HNO₃, and 5.6 M HF-4.5 M H₂SO₄ were used with MIBK as an extractant. The former mixture (HF-HNO₃) was operationally unsatisfactory as it attacked the MIBK and extraction was very poor because a large number of extractions were required before the niobium extraction approached completion. The HF-H₂SO₄ medium was more satisfactory from an operating standpoint, therefore, solution samples were analyzed (Table 5) and standard addition tests carried out on the solution samples (Table 4).

(e) Comparison of Results for Niobium using Different Sample Treatment and Blank Correction Procedures

A number of solution and solid samples of typical sample material were analyzed using different sample treatment and blank correction procedures. These results are shown in Table 5.

TABLE 4

Standard Addition Tests Carried out on Typical Samples

Sample No. EMM- and Sample Type	Niobium Added $\mu\text{g Nb}_2\text{O}_5$	Niobium Found, $\mu\text{g Nb}_2\text{O}_5$				Perchloric Fuming
		Evaporation with Mixed Acids		H_2SO_4 -HF-MIBK		
		Followed by $\text{K}_2\text{S}_2\text{O}_7$ Fusion	Followed by H_2SO_4 Fuming	Not Fused Following Extraction	Fused Following Extraction	
X-Niobium Free Solution	4.80	-	-	4.78 ^c	-	-
	9.00	9.03 ^a	-	-	-	-
373-Ppt'n Feed Solution	2.40	-	-	0.65 ^{bc}	-	-
	3.60	-	-	-	2.32 ^{bc}	-
	6.00	6.16 ^a	-	-	-	6.20 ^c
	7.20	-	7.37 ^a	-	-	-
384-Ppt'n Feed Solution	2.40	-	-	4.49 ^{bc}	-	-
	3.60	-	3.50 ^a	-	-	-
	6.00	5.73 ^a	-	-	-	5.98 ^c
517-Ppt'n Feed Solution	2.40	-	-	-	0.84 ^{bc}	-
	5.40	5.20 ^a	-	-	-	-
	3.60	-	3.50 ^a	-	-	-
	6.00	-	-	-	-	6.00 ^c
	6.75	6.77 ^a	-	-	-	-
967-PZT 95 Solid, Niobium-Free	6.00	-	-	-	-	6.08 ^c
968-PZT 95 Solid	6.00	-	-	-	-	5.95 ^c
969-PZT 95 Solid	6.00	-	-	-	-	6.20 ^c
970-PZT 95 Solid	6.00	-	-	-	-	5.95 ^c

- a - niobium added prior to evaporation and fusion or fuming step
b - white precipitate formed during extraction
c - niobium added immediately before colorimetric finish

TABLE 5

Determination of Niobium in Ceramic Sample Materials using
Different Sample Treatment and Blank Correction Procedures

Sample No. EMM- and Sample Type	Niobium Content Estimate % or g/l Nb ₂ O ₅	Sample Treatment						HF-H ₂ SO ₄ - ^b MIBK Extraction % or g/l Nb ₂ O ₅
		None	HClO ₄ Fuming	H ₂ SO ₄ Fuming	Acid Fuming and Pyrosulphate Fusion ^a			
		Proc A % or g/l Nb ₂ O ₅	Proc A % or g/l Nb ₂ O ₅	Proc A % or g/l Nb ₂ O ₅	Proc A % or g/l Nb ₂ O ₅	Proc B % or g/l Nb ₂ O ₅	Proc C % or g/l Nb ₂ O ₅	
X-Niobium-Free Solution	-	<0.002	-	-	0.046	0.000	-	<0.0003
373-Ppt'n Feed Solution	0.25	0.068	0.13 0.26 ^c	0.26	0.29	0.28	0.27 0.29 ^d	0.3
384-Ppt'n Feed Solution	0.50	0.11	-	0.50	0.53	0.51	0.49 0.52 ^d	0.42
517-Ppt'n Feed Solution	0.75	0.15 0.30 ^c	0.29 0.41 ^c	0.69	0.73 0.75 ^c	0.68	0.70 0.75 ^d	0.60
967-PZT 95 Solid, Niobium- Free	-	-	<0.002	0.009	-	-	<0.0001	-
968-PZT 95 Solid	0.5	-	0.33	0.45	-	-	0.46 0.49 ^d	-
969-PZT 95 Solid	1.0	-	0.68	0.92	-	-	0.94 1.00 ^d	-
970-PZT 95 Solid	1.5	-	0.95	1.32	-	-	1.35 1.44 ^d	-
1693-Lot N-5 Spray Dried at 700°C	1.0- 1.5	-	-	1.25	-	-	1.30 1.38 ^d	-
1694-Lot N-6 Organic Treat- ment - Dried at 700°C	1.0- 1.5	-	-	1.28	-	-	1.33 1.42 ^d	-

a - Proc A - reagent blank correction
 Proc B - reagent + pyrosulphate blank correction
 Proc C - reagent + pyrosulphate + matrix blank
 correction

b - followed by pyrosulphate fusion
 c - double amount of thiocyanate present
 d - calculated using correction factor
 established from standard recovery
 tests on synthetic samples (Table 3).

No account taken of moisture present in the
 solid samples.

RESULTS AND DISCUSSION

It was found necessary to pretreat solution samples by heating with nitric acid and taking to sulphuric fumes before the colorimetric finish. Results were low if only perchloric acid fuming had been done and were even lower if the sample had not been treated at all (Table 5).

Although some solid samples dissolved following mixed acid treatment to sulphuric fumes, the most satisfactory general dissolution procedure was found to be pyrosulphate fusion of the dried salt after evaporating the sample with sulphuric acid to dryness. Grimaldi⁽³⁾ has found that the presence of pyrosulphate (in much larger quantities than we had in the colorimetric finish) diminishes the intensity of the niobiumthiocyanate color. It was found in our work that the quantity of pyrosulphate present gave a positive blank, the amount of which must be known and a correction made for its contribution. Also, the sample matrix contributed to the blank effect and must be corrected for by using a suitable correction procedure or results could be high or low depending on the correction made (Table 2):

Attempts to avoid this matrix blank effect by using solvent extraction techniques to separate niobium from contaminants were unsuccessful. Results of tests on samples to which standard additions had been made were very erratic (Table 4), but results obtained on the samples alone were lower in all cases than those obtained from

using a direct procedure (Table 5). Extraction with MIBK from HF-H₂SO₄ medium was more successful than from HF-HNO₃ medium but precipitation problems with lead sulphate prevented its successful use. An HF-HCl system(5,6) and a hydrochloric system alone(7) have been used for this type of separation but were not tested here due to time limitations.

In standard addition tests carried out on solution samples, recoveries were quite good following pyrosulphate fusion and/or sulphuric fuming (Table 4). Similar standard addition tests were not carried out on the solid samples in sulphate medium. However, results from the standard recovery tests on prepared synthetic samples (which duplicated the actual samples) indicated that, when a full correction was made for the sample matrix blank, recovery of the niobium (in the niobium to contaminant ratio found here) would be low by an average of about 6% (Table 3).

RECOMMENDATION

Care must be taken to use a proper blank correction and to apply a correction technique based on standard addition tests on synthetic mixtures or on actual samples. For best accuracy, therefore, it is recommended that one of the following techniques be used:

- (a) apply a correction factor based on the results found using niobium-recovery tests similar to those described above (Table 3);

- (b) add a range of niobium standards to synthetic samples made up to duplicate the sample matrix and calculate results from a standard curve drawn up on this basis; or,
- (c) make standard additions of niobium to the niobium-bearing ceramics and calculate results according to the recovery obtained.

Of the above techniques, (a) or (b) are considered to be the better, providing accurate knowledge of the sample composition is available.

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