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Quantitative determination of tantalum in niobium by neutron activation analysis

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A method was devised for the determination of Ta both in mixtures of $NbCl_5-TaCl_5$ and in mixtures of $ANbCl_6-ATaCl_6$, where A = Na, K, Rb, or Cs. The method involves neutron activation analysis of $Nb_2O_5-Ta_2O_5$ samples prepared by conversion of the chlorocompounds.

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On a conçu une méthode de détermination du tantale dans les deux mélanges suivants: $NbCl_5-TaCl_5$ et $ANbCl_6-ATaCl_6$ où A = Na, K, Rb ou Cs. La méthode implique l'analyse pour l'activation de neutrons des échantillons du $Nb_2O_5-Ta_2O_5$ préparés par la transformation des composés chlorés.

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During the course of an investigation to test the proposition that it is possible to separate Ta from Nb by the reaction of vapour mixtures of $NbCl_5-TaCl_5$ with either solid or molten ACl, where A = Na, K, Rb, or Cs, it became necessary to devise a technique for determining the concentration of Ta both in mixtures of $NbCl_5-TaCl_5$ and in mixtures of $ANbCl_6-ATaCl_6$, where the Ta concentration ranged from 0.5 to 10 wt.% on a metal–metal basis with Nb (1). Quantitative analysis of tantalum–niobium systems is difficult by standard chemical methods. X-ray fluorescence has been used successfully under carefully controlled conditions (2–6). To avoid potential problems such as matrix effects and the high dependence on the method of sample preparation inherent in this technique neutron activation analysis was chosen for the present work.

Sample Preparation

Since the chlorocompounds of niobium and tantalum hydrolyse readily, it was necessary to convert them to a stable form, in this case their pentoxides, by adding the salt mixtures to water, boiling for 5 min, and then evaporating to dryness. The cake which formed was ground to a powder which was then added to water, boiled for 5 min, and evaporated to dryness. Prior to this second evaporation, in the analysis of $ANbCl_6-ATaCl_6$ mixtures only, filtration was performed to separate the alkali-metal chloride presumed to have dissolved in the water. The dried cake was ground to a powder, added to concentrated NH_4OH, and evaporated to dryness. After grinding, the product was ignited in a platinum crucible at 900°C.

X-ray powder diffraction patterns verified that the hydrolysis of the pentachlorides to the pentoxides was complete, i.e. that

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Nb_2O_5 and Ta_2O_5 were formed. Furthermore, to prove that the hydrolysis of $AMCl_6$ proceeded according to the reaction

$$[1] \quad 2AMCl_6 + 5H_2O \rightarrow M_2O_5 + 10HCl + 2ACl$$
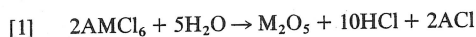
the filtrate, which was assumed to contain dissolved ACl, was evaporated to dryness. The X-ray powder pattern of the dried filtrate was identified as that of ACl in each case.

A reliable procedure for sample preparation having been established, a set of standards spanning the range 0.1 < wt.% Ta < 10 was made. First, large quantities of $NbCl_5$ and $TaCl_5$ were hydrolysed separately to make Nb_2O_5 and Ta_2O_5. The materials were screened through a 200 mesh sieve, and the appropriate amounts were mixed by a novel technique. Campbell and Carl (3) and Mitchell (4) have reported that mixed $Ta_2O_5-Nb_2O_5$ samples can be prepared by co-precipitation from hydrofluoric acid solutions. In this laboratory the oxides were found to be extremely difficult to dissolve, an observation made also by Campbell and Carl (3). A different method was used to mix the oxides.

The two powders were put into a 600 mL beaker containing approximately 300 mL of water. The water was heated to a violent boil and for about 10 min was stirred with a glass rod. The water was evaporated, and the powder was passed again through a 200 mesh sieve. Samples of the same nominal composition, some having been prepared by co-precipitation and others "wet mixed", were compared by neutron activation analysis. Results were within limits of statistical error of one another. As well, several samples from the same batch of wet-mixed material were analyzed to determine if the particle distribution was random. Again, the results agreed within statistical limits of error.

Results

The powdered samples weighed approximately 300 mg and were contained in polyethylene vials. They were irradiated in the SLOWPOKE nuclear reactor at this university in a neutron flux of 1.0×10^{11} n/cm^2 s for 60 s. After a decay time of 60 s the irradiated samples were counted for 300 s. Thus, the total time to analyze a sample was 7 min. Mea-

surements of γ-ray activities were made with a Canberra Ge(Li) detector coupled through a 452 Ortec spectroscopy amplifier to an 8100 series, 4096 channel Canberra analyzer. The detector has a nominal relative counting efficiency of 6.7% and a FWHM resolution of 1.9 keV for the 1332 keV γ-ray of ^{60}Co. γ-Ray peak intensities were evaluated by automatic analyzer integration of suitable manually selected spectral regions of interest at and near each peak.

Every time a set of samples was measured, the entire set of standards was also irradiated. While both Nb and Ta were counted, the Nb results were not found to be useful. Below about 3 wt.% Ta there was no discernible trend in the Nb results. Although self absorption effects in samples high in Ta give rise to curvature in the calibration curve, the measurements of the standards were best represented for our purposes by two least-squares lines, one for Ta concentrations less than 4 wt.% and one for Ta concentrations between 4 wt.% and 10 wt.%. The elemental Ta content of a sample was determined by comparison with the standard line recorded on the same day.

Typical results are the following. In the range, 0 < wt.% Ta < 4,

$$[2] \quad \text{wt.\% Ta} = -(0.20 \pm 0.07) + (117 \pm 3) \times 10^{-6} n$$

where n represents the number of counts s^{-1} g^{-1} of oxide sample. The correlation coefficient[2] was $r = 0.9986$, and standard error of estimate was $\hat{S}_{y,x} = 0.08$. In the range 4 < wt.% Ta < 10,

$$[3] \quad \text{wt.\% Ta} = -1.07 \pm 0.24 + (142 \pm 4) \times 10^{-6} n$$

The correlation coefficient was $r = 0.9996$, and the standard error of estimate was $\hat{S}_{y,x} = 0.12$.

The corresponding amount of Ta_2O_5 present in the sample was then calculated, and the difference between this and the total mass of the sample was presumed to be the mass of Nb_2O_5. From the latter figure the mass of elemental Nb was calculated. Finally, the Ta concentration was reported as wt.% Ta in Ta–Nb metal. It has an absolute error of estimate of less than 0.1 wt.% over the range of interest. The lower limit of detection for this method using samples such as these described herein was determined to be 330 ppm Ta in Nb on a metal–metal basis (8).

This method is accurate provided that the sample consists of only Nb_2O_5–Ta_2O_5. As a precaution,

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[2]Correlation coefficients are determined to the 67% confidence level.

TABLE 1. Nuclear data for sample analysis (7)

Element	Isotope measured	Half-life	γ-ray (keV)
Nb	^{94m}Nb	6.6 min	871.1
Ta	^{182m}Ta	16.2 min	146.7, 171.7
Na	^{24}Na	15 h	1368.4
K	^{42}K	12.52 h	1524.7
Rb	^{86m}Rb	1.02 min	555.8
Cs	^{131m}Cs	3.15 h	127.4
Cl	^{38}Cl	37.29 min	1642.0

then, the entire γ spectrum of each sample was scanned to detect the presence of any other metals. In samples prepared from the pentachloride mixtures of $NbCl_5$–$TaCl_5$ only Ta and Nb were found. However, samples prepared from $ANbCl_6$–$ATaCl_6$ mixtures contained small but measurable amounts of alkali metal representing less than 5% of the total mass of the sample. Since the chlorine content was below the lower limit of detection which was approximately 100 μg in those samples, it was concluded that the alkali metal was not present in the form of its chloride. So, it was assumed that the alkali metal was present as oxide or, more likely, niobate or tantalate, and the appropriate correction was made to the Ta concentration reported. Table 1 shows the isotope which was measured for each element. For tantalum both the tabulated γ-ray peaks were routinely counted. With the spectrometer employed, the 172 keV peak was approximately 25% greater than that at 147 keV, and the bremsstrahlung in the region of the former is approximately 30% weaker. Indeed, the results for the peak at 172 keV proved to be more reproducible and, thus, were favoured in the quantitative determination of tantalum.

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