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Neutron activation analysis of the sodium tungsten bronzes

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Iowa State University of Science and Technology
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**NEUTRON ACTIVATION ANALYSIS OF THE SODIUM TUNGSTEN
BRONZES**

by

Robert John Reuland

**A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY**

Major Subject: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

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**Iowa State University
Of Science and Technology
Ames, Iowa**

1963

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INTRODUCTION

Neutron Activation Analysis

The method of activation analysis consists of the determination of the weight of an element in a sample by measuring the radioactivity induced in the element by some type of nuclear bombardment. The intensity of the induced radioactivity is directly proportional, other things being equal, to the weight of the element determined and is, of course, independent of the state of chemical combination of the element. Neutron activation analysis utilizes neutrons as the activating particle in the nuclear bombardment. The source of these neutrons is generally the nuclear reactor, although in recent years the portable, linear accelerator has received increased application as a neutron source. In some instances, activation with low yield neutron sources such as RaBe or SbBe sources is possible.

The discovery of the activation analysis method dates back nearly to the discovery of artificial radioactivity itself. In 1936, von Hevesy and Levi (1, 2) determined 0.1% dysprosium and europium in rare earth mixtures using a RaBe neutron source. In 1938, Seaborg and Livingood (3) analyzed iron for small amounts of gallium, activating the gallium with deuterons accelerated in a cyclotron. These investigations occurred before the advent of the nuclear reactor in 1942. In 1947, Tobias and Dunn (4) began to use reactor neutron fluxes as the means of activation in their analysis for trace elements in biological tissue. It has been in the last decade, however, that activation analysis has had widespread application. This can be attributed in part to the availability of nuclear reactors and the appearance of the portable, linear accelerator, and to the establishment

and refinement of the techniques of gamma-ray scintillation spectroscopy. Several excellent reviews of activation analysis (5-10) have appeared in the literature as well as two thorough series of bibliographies (11-16). Although the emphasis in neutron activation analysis has been on trace analysis (<0.001%), minor constituent analysis (0.001-1%) is possible and has been reported in a number of instances.

For the case in which the isotope 1 of the element to be determined is transmuted to radionuclide 2 which decays with a decay constant λ_2 to the stable isotope 3, the induced radioactivity is given by

$$A_2 = \frac{\sigma_1 \phi W (6.02 \times 10^{23}) \theta_1}{M} (1 - e^{-\lambda_2 t}) e^{-\lambda_2 T} \quad (1)$$

where ϕ is the neutron flux, σ_1 and θ_1 are the activation cross section and isotopic abundance of 1, W and M are the weight and atomic mass of the element being determined, and t and T are the bombarding and cooling times, respectively. Thus, it is evident that the weight W of the element can be determined from the measured absolute disintegration rate A_2 once the neutron flux is known.

In the derivation of the activation equation, the neutron flux is assumed to be constant. That this is not always true leads to perhaps the most serious obstacle to the activation method. The presence of a nuclide in the matrix of the sample with a high absorption cross section causes attenuation of the neutron flux. Consequently a smaller neutron flux is experienced by those atoms located within the sample than by those close to the surface. This self-shielding or self-shadowing effect is frequently encountered in resonance activation in which the resonance

absorption cross section of the element to be determined is often very high. The result is a literal "self"-shielding effect. The self-shielding is usually evaluated experimentally although semi-empirical calculations have been made (17). It is often possible to minimize the effect of an inhomogeneous neutron flux by a reduction in the size of the sample or by dilution with an inert matrix. In some cases, neutron flux variations may be corrected using internal standards (18-20). Less frequently, the effect is compensated by a judicious choice of the neutron flux monitor, one whose composition closely approximates the composition of the sample.

The absolute method of neutron activation analysis, which requires a knowledge of the absolute disintegration rate and the neutron flux, is in fact difficult to apply. Besides the necessity of converting the measured counting rate to the absolute disintegration rate, the method is dependent upon the accuracy with which the absolute cross sections are known, and this accuracy is often not sufficient. As a result, a comparison method of neutron activation analysis is usually applied. This method involves the simultaneous bombardment of the sample and a suitable standard containing a known amount of the element to be determined. A standard with approximately the same composition as the sample is desirable in instances when self-shielding effects are suspected. In the absence of self-shielding, the specific activities in the sample and standard of the element analyzed are given by

$$\left[\frac{A_2}{We^{-\lambda_2 T}} \right]_{\text{sample}} = \frac{\sigma_1 \phi (6.02 \times 10^{23}) \theta_1}{M} (1 - e^{-\lambda_2 t}) = \left[\frac{A_2}{We^{-\lambda_2 T}} \right]_{\text{standard}} \quad (2)$$

When the radioactivity of nuclide 2 in both the sample and standard is counted under identical conditions, the effects of geometry and counter efficiency are normalized and the absolute disintegration rate can be replaced with the observed counting rate R_2 . After the observed counting rates are corrected for decay, if necessary, the above expression reduces to

$$\left[\frac{R_2}{W} \right]_{\text{sample}} = \left[\frac{R_2}{W} \right]_{\text{standard}} \quad (3)$$

Thus it is obvious that an analysis of the sample is possible from a measurement of the counting rates of nuclide 2, knowing only the amount of the element being determined that is present in the standard.

Clearly, the sensitivity of neutron activation analysis is a function of the activation cross section, the neutron flux, and the half-life of radionuclide 2 (The latter as a result of the relation $\lambda_2 = \frac{0.693}{[t_{1/2}]_2}$). In general, it increases with increasing cross section and flux and decreasing half-life. Too high a cross section, however, may present self-shielding difficulties while too short a half-life may complicate or preclude counting, particularly if a chemical isolation of the radionuclide 2 is necessary. Nevertheless, sensitivities as high as 10^{-11} - 10^{-12} gram are not unusual. Calculated and experimental sensitivities have been reported by several investigators for the various elements (5-10, 21, 22).

The radionuclides produced in the activation process have unique decay characteristics such as half-life and gamma-ray energy. Therefore, the analysis is highly specific. The specificity of the method has been greatly increased by the modern techniques of gamma-ray

scintillation spectroscopy. As a result purely instrumental, or non-destructive neutron activation analysis in which no chemical separations are employed has assumed increased importance and popularity. Nevertheless, it is still necessary in many instances to isolate the desired radionuclide from the radioactive interferences. This is particularly true in trace analysis, where the radioactivity of an activated matrix element often completely swamps that of the element being determined. In this case the conventional, or destructive neutron activation analysis method, which involves radiochemical separations, must be used.

The self-sustaining fission of U^{235} in the nuclear reactor provides the most prolific source of neutrons for activation analysis. Thermal neutron fluxes as high as 5×10^{14} neutrons/cm²-sec are possible. Such high fluxes are desirable for trace activation analysis in which high sensitivity is required.

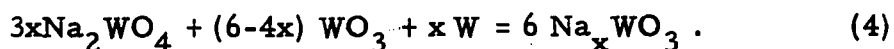
Neutrons are produced in the linear accelerators by the (d, n) nuclear reaction with tritium. The deuterons are accelerated through 150 kev and strike a titanium-tritium target, producing yields of 14 Mev neutrons in excess of 10^{10} neutrons/sec. These neutron generators thus provide an ample and convenient source for fast neutron activation analysis, that is, analysis utilizing (n, p), (n, α) and (n, 2n) activation as contrasted with (n, γ) activation by thermal neutrons. Radioactive sources such as RaBe or SbBe sources are possible due to the low (α , n) and (γ , n) thresholds of beryllium and provide neutron fluxes of 10^5 - 10^6 neutrons/cm²-sec. These sources are generally not of sufficient intensity to provide sensitivities in the parts per million range and therefore have limited

application.

The Sodium Tungsten Bronzes

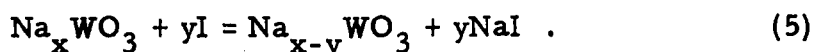
The sodium tungsten bronzes are in fact nonstoichiometric sodium metatungstate. For over one hundred years following their discovery by Wöhler (23, 24) in 1823, a great number of compounds of complicated formulae were reported as sodium tungsten bronzes. In 1935, however, it was found that all the tungsten bronzes correspond to the formula Na_xWO_3 for which the value of x could vary from one to zero (25, 26). For $x > 0.5$, the sodium tungsten bronzes exhibit metallic properties of luster and electrical conductivity and it was this that was responsible for their being called "bronzes".

The original preparation of sodium tungsten bronze by Wöhler involved hydrogen reduction of a sodium tungstate melt. Since that time, several other methods of preparation have been reported. Straumanis (27) and Brimm et al. (28) prepared the bronze by slowly heating sodium tungstate, tungsten(VI) oxide, and tungsten (as the reducing agent) in a vacuum to 950°C followed by slow cooling, the reaction being,



The x value of the bronze could be predicted from the actual ratio of the reactants only in the case of the lowest values of x . To prepare higher values of x , an excess of sodium tungstate over that required by equation 4 was necessary. Brown and Banks (29) investigated the conditions under which the starting materials in equation 4 entered completely into the formation of the bronze. They found that the products of the reaction

represented by the equation do have compositions corresponding to the stoichiometric composition of the reactants, provided the reactants are heated for long periods of time (500 hours) at temperatures (500-750°C) at which they remain solid. Under these conditions, bronzes occur within the range $\text{Na}_{0.30}\text{WO}_3$ to $\text{Na}_{0.85}\text{WO}_3$. Solid tungsten bronzes with $x > 0.85$ can be prepared (27, 29) by reacting bronzes of high x value with sodium vapor at high temperatures in a vacuum. This appears to be the most promising method of obtaining the end member of the series, NaWO_3 , which has not yet been prepared and is perhaps unstable (29). Sodium tungsten bronzes with $x < 0.3$ can be prepared (27) from bronzes of higher x value by reaction with iodine at high temperature (800°C) in a vacuum, according to the reaction,



Single crystals of the sodium tungsten bronzes have been prepared (29-33) by cathodic reduction of sodium tungstate-tungsten(VI)oxide melt. It was found empirically (33) that the x value of the bronze depends on the WO_3 concentration of the melt and that, as the latter is decreased from 50 to 20 mole per cent, the value of x changes from 0.5 to 0.92. Attempts to grow crystals with an x value greater than 0.92 by cathodic reduction were unsuccessful.

The sodium tungsten bronzes with x from about 0.4 to slightly below one were reported to crystallize in cubic symmetry (25, 26, 34). For $x < 1$, the lattice contains $(1-x)$ vacant interstices. Bronzes with lower symmetry than cubic exist for lower values of x (35-37). The phase change, from cubic to tetragonal, occurs with $x \sim 0.4$, the exact x value

depending upon the method of preparation of the bronze. Interestingly, electrostatic energy calculations (38) indicate that cubic sodium tungsten bronze should be unstable or metastable below $x = 0.35$.

More recently, however, Ingold and DeVries (39) reported a temperature range over which a twinned phase exists for the sodium tungsten bronzes with $x > 0.5$. The optical behavior of the twinned phase can be described in terms of a tetragonal cell with c/a in the range 0.990-1.000. Shanks¹ has speculated, however, that this observation results from tungsten(VI)oxide layers that form on the surface of the bronzes and which are known to exhibit this twinning behavior.

The electronic properties of the sodium tungsten bronzes are of particular interest. Magnetic susceptibility measurements (40, 41) suggest that the conduction electrons approximate an electron gas. Measurements of the Hall coefficient (42) indicate that, for the cubic bronzes, one nearly free electron is contributed to the conduction band per sodium atom. Thus, control of the number of conduction electrons can be accomplished without changing the crystalline symmetry simply by controlling the sodium concentration. Early investigations (42, 43) showed that the resistivity of single crystals of the bronzes, when plotted as a function of the sodium concentration x in the range $0.53 < x < 0.85$, exhibited an anomalous minimum at $x = 0.7-0.75$ which was not adequately explained. A subsequent investigation (44) into the cause of the minimum indicated that sample homogeneity was the most important factor. It now

¹Shanks, H. R., Ames, Iowa. Existence of twinned phase for sodium tungsten bronzes. Private communication. 1962.

appears almost certain that no minimum exists in the curve of resistivity versus sodium concentration if the crystals are selected to be electrically homogeneous. The nuclear magnetic resonance of Na^{23} in the sodium tungsten bronzes measured over a range of sodium concentrations from $x = 0.56$ to $x = 0.89$ exhibited essentially no Knight shift (45). This implies a negligible concentration of conduction electrons at the sodium positions. The proposed explanation (46) assumes that the conduction band is one arising from the tungsten orbitals and that the electrons contributed by the sodium atoms occupy these orbitals.

A study of the absorption spectra of the sodium tungsten bronzes between 3350 and 12500Å has been made by the diffuse reflectance method (29). When bronzes were considered as solid solutions of tungsten(VI)-oxide in the hypothetical NaWO_3 , $\text{Na}_x(\text{W}^{\text{VI}}\text{O}_3)_{1-x}(\text{W}^{\text{V}}\text{O}_3)_x$, attempts to fit the absorption data to a standard Beer's law treatment, or a reasonable deviation therefrom, were not successful. The more recent model, based on magnetic susceptibility, Hall coefficient, and resistivity measurements, is of sodium dissolving in tungsten(VI)oxide with the subsequent formation of sodium ions and an electron gas within the tungsten(VI)oxide lattice. The x "extra" electrons per mole (over the number for WO_3) distributed throughout the lattice are delocalized in energy bands somewhat similar to those of genuine metals. The bronzes were therefore treated as typical metals with perfectly free electrons in an attempt to account for the absorption spectra. However, the reflectance from the powdered samples that were employed was too complex to be simply related to their metallic behavior.

A contraction of the lattice with decreasing sodium concentration has been observed by several investigators (26-29) throughout the cubic range of the sodium tungsten bronzes. A linear relation was found to exist between the lattice parameter a_0 and the sodium concentration x . There is some question as to the lattice parameter for NaWO_3 , that is, $x = 1.0$. Nevertheless, the equation of Brown and Banks (29)

$$a_0 (\text{\AA}) = 0.0819x + 3.7846 \quad (6)$$

is considered the most accurate. The decrease in sodium concentration is also accompanied by a continuous change in color of the bronze. For x close to 1, the color is golden yellow. As x decreases the color deepens through red and violet until it is dark blue for $x = 0.3$.

Chemically, the sodium tungsten bronzes are extremely unreactive. Their chemical inertness is manifested in their insolubility in water and resistance to all acids. They do, however, possess reducing properties, reducing ammoniacal silver nitrate to metallic silver. They can likewise be oxidized by oxygen in the presence of base to give tungstates.

Little has been reported regarding their chemical analysis. Such analyses are rather troublesome due to the difficulty of bringing the bronzes into soluble form. Spitzin and Kaschtanoff (32) oxidized the sodium tungsten bronzes to tungstates in an oxygen stream at 500°C and then decomposed the tungstates to volatile tungsten oxychloride and sodium chloride at $500\text{-}550^\circ\text{C}$ with hydrogen chloride gas. The sodium content was determined from the weight of the sodium chloride residue. Magnéli (47) decomposed the sodium tungsten bronzes by heating with ammonium peroxydisulfate after which the melt was dissolved with water

and the sodium ions isolated by passing the solution through an Amberlite IR 100 ion exchanger. The amount of sodium was determined by titrating the eluate, sodium chloride, for the equivalent amount of chloride according to the method of Mohr. Brimm et al. (28) have determined the sodium content by digesting the bronze with ammonium sulfate and sulfuric acid and precipitating the sodium as sodium uranyl zinc acetate. The reducing properties of the bronzes have been utilized by Brown and Banks (29). The finely powdered bronze was decomposed with ammoniacal silver nitrate, an equivalent of silver metal being deposited for each equivalent of sodium in the bronze. The silver was determined by the Volhard method after dissolving in 0.3N nitric acid. The precision of these last two analyses was such that there was an error of about ± 0.02 in the value of x (2-7%, depending on the value of x). Wold¹ has developed a weight-gain technique for bronzes in the cubic range. The bronze is heated in air at 800°C and the weight gain represents " W^V " or sodium present. The results of this method were compared with the results obtained by deduction from lattice parameter measurements with an agreement to within 1%. Investigations by Raby² and Banks (48) are in progress which utilize bromine trifluoride in the complete analysis of alkali tungsten bronzes. Also in progress is an emission spectrometric technique³ in which the powdered sodium tungsten bronze and a rubidium

¹Wold, A., Lexington, Massachusetts. Sodium analysis of sodium tungsten bronzes. Private communication. 1962.

²Raby, B. A., Ames, Iowa. Total analysis of alkali tungsten bronzes using bromine trifluoride. Private communication. 1961.

³Wendt, R. H., Ames, Iowa. Emission spectrometric analysis of sodium tungsten bronzes. Private communication. 1961.

chloride internal standard are excited by a d-c arc. The photometric determination of the intensity ratios of selected line pairs yields a linear function of the concentration and intensity. Still, the most convenient and reliable method for measuring the sodium concentration of the cubic sodium tungsten bronzes is the deduction of x from measurement of the lattice parameter.

Neutron Activation of the Sodium Tungsten Bronzes

Interest in the sodium tungsten bronzes, particularly the solid state physicist's interest in their electronic behavior, has stimulated this and other investigations of modern methods of their analysis. Especially, there is a need for a method of analysis of sodium concentrations with $x < 0.4$, that is, in the non-cubic range, where deduction from the lattice parameter measurement is not possible and for which no accurate method is presently available. The extreme inertness of the bronzes requires unusual, if not drastic, chemical procedures, such as fluorination. A spectrometric method, which involves conventional spectrochemical procedures would be preferred for its convenience.

The feasibility of neutron activation analysis of the sodium tungsten bronzes, as well as possible interferences, can be ascertained from a consideration of the nuclear properties (49) of the bronze constituents subject to activation by thermal neutrons. These properties are summarized in Table 1.

It can be seen that the thermal neutron activation cross section of Na^{23} and the half-life of Na^{24} are such that adequate activation is

Table 1. Nuclear properties of the bronze constituents subject to activation by thermal neutrons

Target nuclide	Abundance (%)	Activation cross section (barns)	Atomic absorption cross section (barns)	(n, γ) reaction product	Product half-life
Na Na ²³	100	0.54	0.5	Na ²⁴	15.0 h
W W ¹⁸⁰	0.135	30	19.2	W ¹⁸¹	140 d
W ¹⁸²	26.41	19		W ^{183m}	5.5 s
W ¹⁸³	14.4	10.9		W ¹⁸⁴	stable
W ¹⁸⁴	30.64	2.0		W ¹⁸⁵	74 d
W ¹⁸⁶	28.41	34		W ¹⁸⁷	24.0 h
O O ¹⁶	99.759		$< 2 \times 10^{-4}$	O ¹⁷	stable
O ¹⁷	0.037			O ¹⁸	stable
O ¹⁸	0.2039	0.00022		O ¹⁹	29.4 s

possible with a neutron source of moderate intensity. Secondly, W¹⁸⁷ is the only interference anticipated when the bronze is exposed to a thermal neutron flux for a duration necessary to sufficiently activate the sodium.

It happens, however, that the magnitude and nature of the W¹⁸⁷ interference present a serious obstacle to the analysis of the bronze. For the case of a tetragonal sodium tungsten bronze with $x = 0.1$ bombarded for 10 minutes in the thermal flux of a reactor, the ratio of the W¹⁸⁷ activity to the Na²⁴ activity is calculated by Equation 1 to be 120.

Gamma-rays of the following energies are associated with the decay of W¹⁸⁷(49): 72, 136, 206, 226, 249, 482, 510, 552, 621, 627, 686, 775, and 866 kev. The gamma-ray scintillation spectrum of W¹⁸⁷ is given in

Figure 1. In the decay of Na^{24} gamma-rays of 1370 and 2750 keV are emitted with equal intensity (49). The gamma-ray scintillation spectrum of Na^{24} is given in Figure 2. It would appear that the difference in energy between the highest energy W^{187} gamma-ray and the lowest energy Na^{24} gamma-ray would be sufficient to permit isolation of the Na^{24} activity by energy discrimination. However, this was not the case and even with high resolution scintillation spectroscopy, the $\text{W}^{187}/\text{Na}^{24}$ activity ratio was too great to allow complete separation of the two groups of photopeaks. A large part of the Na^{24} spectrum is superimposed upon the slope of the photopeaks of the highest energy W^{187} gamma-rays. This is clearly illustrated in Figure 3, a gamma-ray spectrum of a tetragonal sodium tungsten bronze (N-2-A) with $x \sim 0.1$. This bronze was bombarded for 10 minutes in a reactor with a thermal neutron flux of 8×10^{10} neutrons/cm²-sec. Thus, the production of W^{187} presents a major interference to the assay of the Na^{24} activity and therefore an impediment to the neutron activation of the sodium tungsten bronzes.

The problem of isolating the Na^{24} activity was approached from the destructive as well as the non-destructive viewpoint of activation analysis in this investigation. Clearly, the difficulty encountered with the destructive method of neutron activation analysis is just that encountered in the conventional chemical analysis of the sodium tungsten bronzes--the bronzes are extremely unreactive.

Two types of destructive analyses were investigated. One involved a high temperature reaction of the bronze with nitrosyl chloride and required inverse isotopic dilution; the other depended upon the reaction of

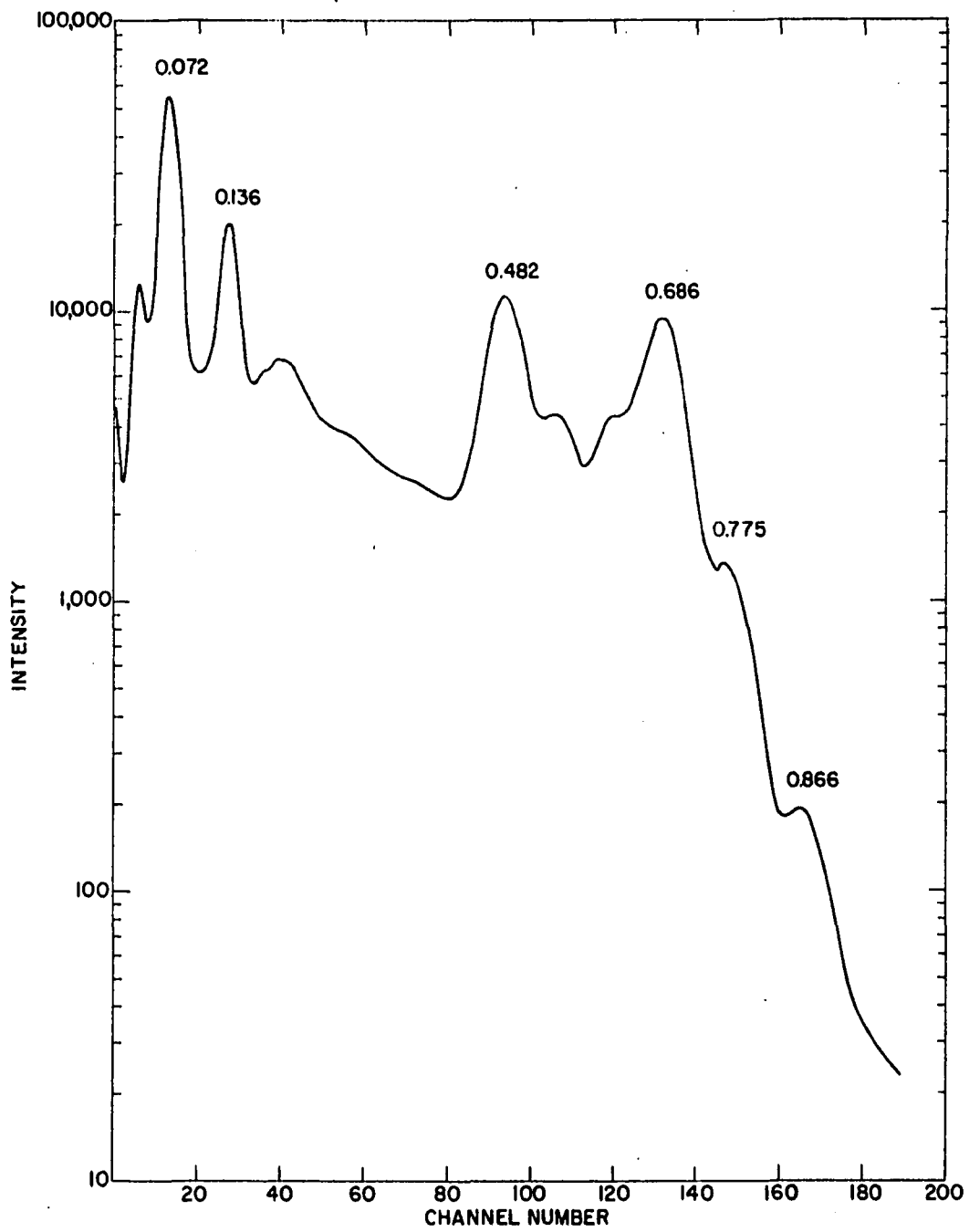


Figure 1. Gamma-ray spectrum of W^{187}

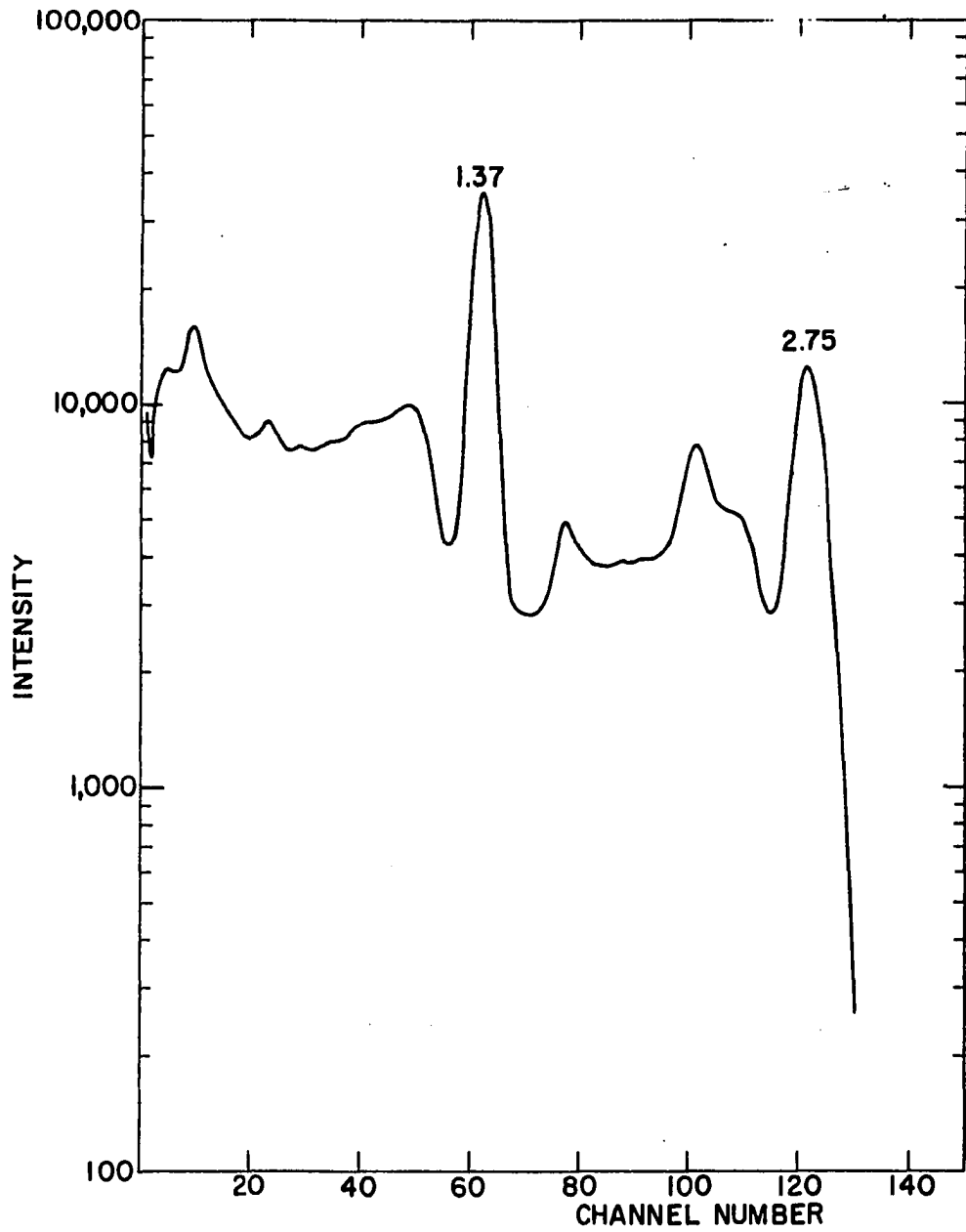


Figure 2. Gamma-ray spectrum of Na^{24}

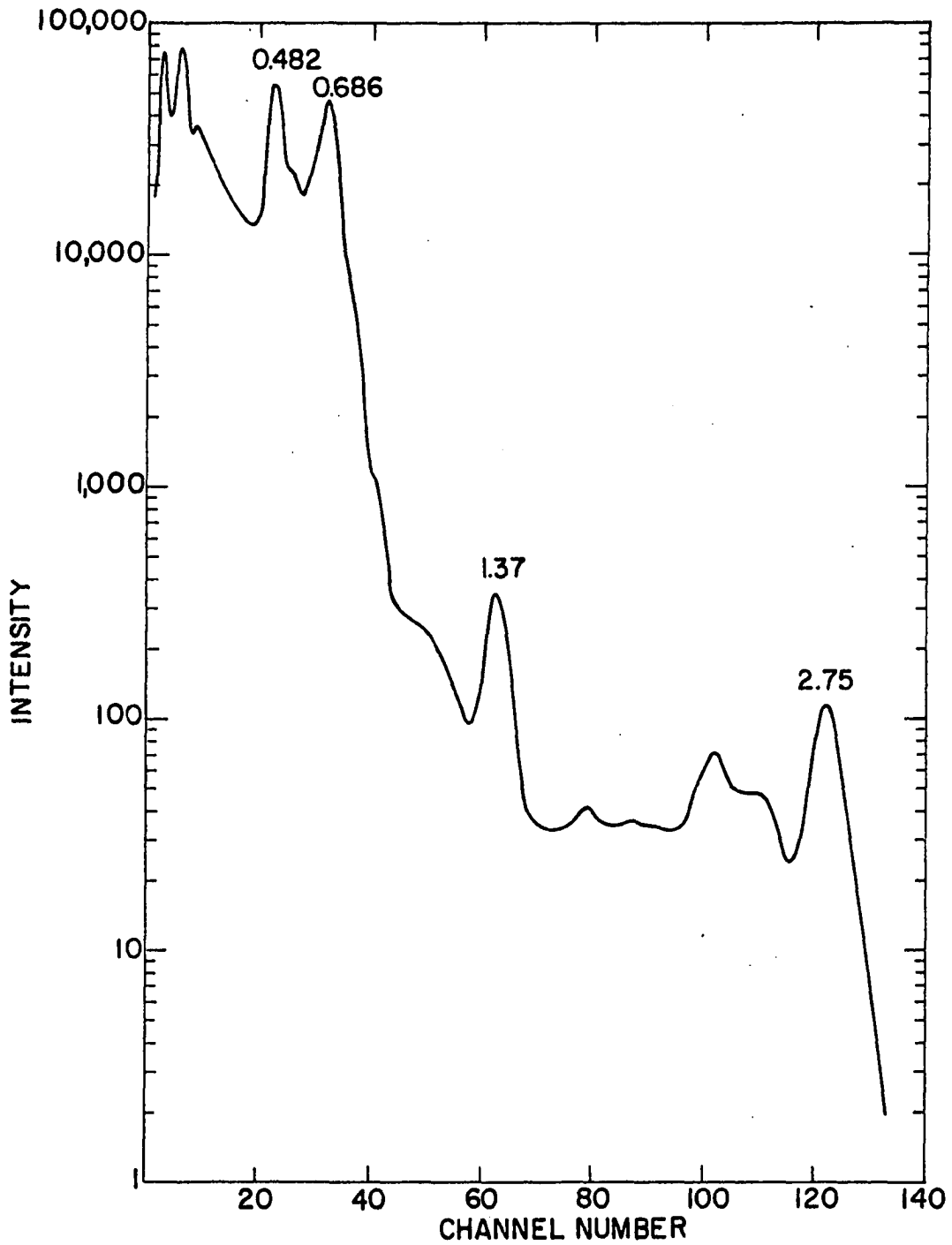


Figure 3. Gamma-ray spectrum of neutron activated Na_xWO_3 (N-2-A)

the bronze with bromine trifluoride.

Likewise, two non-destructive analyses were investigated. One isolated the Na^{24} activity by electronically stripping the W^{187} gamma-ray spectrum from the composite gamma-ray spectrum; the other utilized a simple coincidence counting technique and energy discrimination.

One other non-destructive analysis of the sodium tungsten bronzes was attempted. In this procedure it was hoped that the Na^{24} activity could be isolated in the activation step of the analysis by selectively activating the sodium with neutrons in its resonance energy region. A tungsten filter was employed to prevent, or greatly reduce, resonance activation of the tungsten in the bronze.

Also considered in this investigation was the reproduction of the Brown and Banks equation which relates the lattice parameter of the cubic bronzes to the sodium concentration, using activation analysis for the determination of the latter.

SAMPLE PREPARATION AND INSTRUMENTATION

Preparation of the Sodium Tungsten Bronzes

The composition and structure of sodium tungsten bronze samples studied in this investigation are listed in Table 2. They were prepared by electrolysis of a fused mixture of reagent grade sodium tungstate and tungsten(VI)oxide in glazed ceramic crucibles. The amount of the melt mixture was about 750 grams. The electrolyses were conducted at approximately 700°C with nichrome cathodes and graphite anodes, the current densities being about 20 ma/cm². The sodium concentration of the bronze was varied by varying the amounts of the constituents of the melt. A mixture of approximately 20 mole per cent tungsten(VI)oxide gave high

Table 2. Composition and structure of the sodium tungsten bronzes

Bronze	Lattice parameter (Å)	x	Structure
N-2-A		~ 0.1 ^a	tetragonal
DCL-14-15F ^b	3.8225	0.463	cubic
111-A-1	3.8306	0.562	cubic
124-A-6	3.8305	0.561	cubic
138-A-1	3.8405	0.683	cubic
184-A-1	3.8414	0.694	cubic
116-A-4	3.8495	0.793	cubic
125-A-2	3.8543	0.851	cubic

^aEstimated from method of preparation.

^bObtained from A. Wold.

sodium concentrations; the sodium concentration was then decreased in consecutive runs by adding tungsten(VI)oxide. When the cathode, together with the adhering crystals, was removed from the melt, a layer of the melt protected the crystals from the atmosphere while they cooled to room temperature. This layer was subsequently removed with boiling water. Finally, the crystals were powdered with an agate mortar and pestle.

X-ray Analysis of the Cubic Sodium Tungsten Bronzes

Precise determinations of the lattice parameter a_0 of the cubic bronzes were obtained from Debye-Scherrer powder photographs. A discussion of the accurate determination of cell dimensions is given, for example, by Henry et al. (50). Copper K_{α} radiation was used for the X-ray analysis. Lattice parameters were calculated for both the back and front reflected lines. These parameters were plotted against the function,

$$f(\theta) = \frac{\sin^2 \theta}{2} \left[\frac{1}{\sin \theta} + \frac{1}{\theta} \right], \quad (7)$$

and extrapolated to $\theta = 90^\circ$ at which the absorption error vanishes. In this fashion, the reproducibility of a lattice parameter measurement was better than 0.01%. The actual calculation of the parameters and extrapolation were performed by the IBM 704 Computer located at Madison, Wisconsin. If the Brown and Banks relation between the lattice parameter and the sodium concentration x is exact, the x values for the cubic bronzes analyzed in this investigation were known to within ± 0.003 .

Neutron Source

The neutron source used in this study was the Iowa State University Training Reactor (UTR-10). This is a 10 kilowatt thermal reactor constructed by American-Standard and based on the "Argonaut" design of the Argonne National Laboratory. It is a heterogeneous, tank-type reactor, which is cooled with light water and moderated with water and graphite. The total U^{235} content of the core is ~ 3 kg, present in a 90% enrichment. A pneumatic tube, which terminates against one of the two core tanks, permits convenient access to the highest flux available. At 10 kilowatts, the "rabbit" is exposed to a thermal flux of 8×10^{10} neutrons/cm²-sec. The internal dimensions of the rabbit are $1 \frac{3}{8}$ inches in diameter and $3 \frac{1}{2}$ inches in length.

Counting Equipment

Three gamma-ray scintillation spectrometers were used for the activity measurements, two of which were multi-channel pulse height analyzers while the other was a single-channel pulse height analyzer.

The single-channel analyzer, a Nuclear Chicago Recording Spectrometer, Model 1820, was used only as an energy discriminator for certain of the counting procedures. The selected pulses were counted with a Nuclear Chicago Decade Scaler, Model 186. Either of two detectors was used with this apparatus depending upon the experiment. One was a two-inch by two-inch NaI(Tl) crystal; the other, a two-inch by two-inch NaI(Tl) crystal having a $\frac{3}{8}$ -inch diameter by $1 \frac{1}{2}$ -inch deep well. Both crystals were optically coupled to DuMont 6292

photomultiplier tubes. The crystals were manufactured by the Harshaw Chemical Company.

One of the multi-channel analyzers was a Radiation Counter Laboratories (RCL) 256 Channel Pulse Height Analyzer, Model 20611. The detector used with this spectrometer was a three-inch by three-inch Harshaw NaI(Tl) crystal which was optically coupled to an EMI 9531B photomultiplier tube. The resolution η of this spectrometer, defined as

$$\eta (\%) = \frac{\text{full width at half maximum, } \Delta E, \text{ of Cs-137 line}}{\text{average energy, } \bar{E} (0.662 \text{ Mev})} \times 100, \quad (8)$$

was 9.0%. Besides the cathode ray tube display, the spectral information accumulated in the memory of the analyzer could be read-out with a Hewlett Packard, Model 560A, digital recorder or a Moseley, Model 2D-2, x-y plotter.

The other multi-channel analyzer was a Nuclear Data 256 Channel Analyzer, Model ND 102. The detector used with this spectrometer was a 3 1/2-inch by 3 1/2-inch Harshaw NaI(Tl) crystal having a 3/8-inch diameter by 1 1/2-inch deep well. This crystal was coupled to an EMI 9531B photomultiplier tube. The resolution of this instrument was 8.8%. Besides the cathode ray tube display, data accumulated in the memory of the analyzer could be read-out with an IBM electric typewriter. This spectrometer was used only in the non-destructive analyses of the bronzes.

For certain counting procedures, a Tracer Lab TGC-2 mica end-window Geiger-Mueller tube was used. The pulses were counted with a Nuclear Chicago Decade Scaler, Model 186.

DESTRUCTIVE NEUTRON ACTIVATION ANALYSIS

Nitrosyl Chloride

Introduction

One of the two types of destructive neutron activation analysis of the sodium tungsten bronzes involved a high temperature reaction of the bronze with nitrosyl chloride.

Nitrosyl chloride, NOCl, is a reddish-yellow gas with a normal boiling point of -5.8°C and a freezing point of -61.5°C . It is remarkably stable. Even at 985°C under a total pressure of one atmosphere, dissociation at equilibrium is only 41.8%. It reacts with most of the elements and with an extremely wide range of compounds. Its reaction with water occurs rapidly, forming nitrous and hydrochloric acids. It is commercially available in Monel cylinders. The NOCl used in this investigation was obtained from the Matheson Company.

Many studies of NOCl and its reactions have been reported in the literature, including a review by Beckham et al. (51); but no investigation of the reaction of NOCl with Na_xWO_3 , Na_2WO_4 , WO_3 , or chemically similar substances can be cited. However, Raby¹, in a private communication, reported a high temperature reaction of NOCl and Na_xWO_3 in his investigation of the possible use of NOCl in a gravimetric method of analysis of the sodium tungsten bronzes. The tungsten was removed as the volatile tungsten oxychloride, WO_2Cl_2 , and the sodium was

¹Raby, B. A., Ames, Iowa. Reaction of nitrosyl chloride with sodium tungsten bronzes. Private communication. 1961.

converted to sodium chloride, according to the equation,



However, at the temperature required for the reaction, 700-800°C, some of the NaCl is lost through volatilization which prevented a gravimetric application of the reaction. The loss of the NaCl would present no serious difficulty to the neutron activation analysis of the bronzes; for in this instance the technique of inverse isotopic dilution is applicable which permits calculation of the sodium content of the bronze even though the sodium is not completely recoverable.

Apparatus

The apparatus employed in the NOCl destructive activation analysis of the bronzes is shown in cross-section in Figure 4. The sample, Na_xWO_3 or Na_2WO_4 or both, was weighed into a Coors 0000 glazed porcelain combustion boat and placed in a 9mm (7mm ID) quartz tube. The inlet of the quartz tube was connected to the NOCl cylinder with Tygon tubing. The exit was connected to a gas saturation bottle, likewise with Tygon tubing. The gas saturation bottle contained a dilute aqueous sodium hydroxide solution for decomposing the unreacted NOCl. The quartz tube was placed in a tube furnace together with a chromel-alumel thermocouple. The temperature was controlled with a Powerstat and was monitored with a Brown Portable Potentiometer, Model 126W3, which was connected to the thermocouple.

Preliminary investigations

The preliminary experiments in the NOCl destructive activation

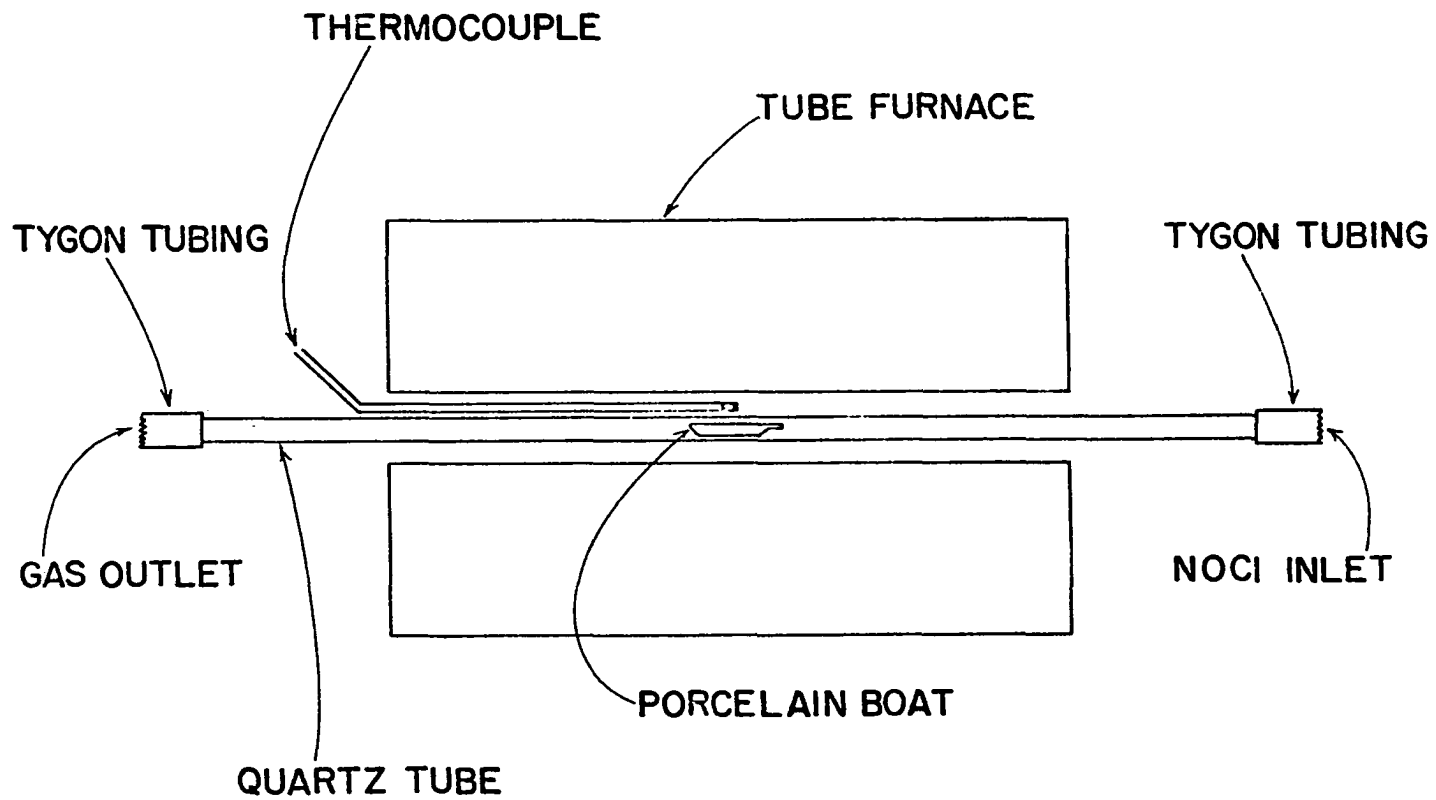


Figure 4. Apparatus used for radiochemical separations involving NOCl

analysis were designed to establish the efficacy of NOCl in the removal of the tungsten from the bronze (and sodium tungstate) and the conversion of the sodium to sodium chloride. The first of these experiments was the reaction of NOCl with sodium tungstate, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. The $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, a certified Fisher reagent, was weighed into a porcelain boat, placed in the apparatus, and heated to 700°C for 1 1/2 hours in an atmosphere of NOCl. A yellow solid, WO_2Cl_2 , condensed on the section of the quartz tube extending out of the furnace. After the reaction, the residue in the boat was weighed and found to be 6.3% less than that calculated from the conversion of the sodium in the $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ sample to NaCl. The residue was then dissolved in water and the chloride determined gravimetrically as AgCl. The difference between the chloride composition determined and that calculated from the weight of the residue, assuming the residue to be only NaCl, was 2.6%. To a large extent, this discrepancy could be explained in terms of experimental errors. Thus, it appeared as though the NOCl was effective in removing the tungsten from the sample and converting the sodium to NaCl, although some of the NaCl was volatilized.

The second experiment also involved the reaction of NOCl and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. The $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ of this experiment was first activated in the maximum flux of the reactor for 15 minutes. A gamma-ray spectrum of the activated $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was accumulated with the RCL pulse height analyzer prior to the chemical separation. The $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was then transferred to a porcelain boat and heated to 750°C for three hours in an atmosphere of NOCl. A gamma-ray spectrum of the activity

of the residue in the boat was accumulated following the separation. These two gamma-ray spectra, accumulated before and after the reaction of the $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ with NOCl , are shown in Figure 5. It is obvious from a comparison of Figures 1, 2, and 5 that a complete radiochemical separation was achieved.

Finally, a sodium tungsten bronze with $x \sim 0.1$ (N-2-A) was treated with NOCl . The bronze was first activated in the reactor in a thermal flux of 8×10^{10} neutrons/cm²-sec for three minutes and then exposed to NOCl for 1 1/2 hours at 800°C. As with the $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, gamma-ray spectra were accumulated before and after the reaction of the bronze with NOCl . Again, the tungsten was completely removed from the sample as indicated by the absence of the characteristic W^{187} photopeaks from the final gamma-ray spectrum.

Self-shielding

The possibility of self-shielding during the irradiation of Na_xWO_3 and Na_2WO_4 was considered because of the high cross section of tungsten. A measure of the extent of self-shielding is obtained by simultaneously activating samples of varying size and plotting the sodium specific activity versus the sample weight. A decrease in the specific activity with increase in the sample weight, all other things being equal, is indicative of self-shielding. Two such experiments were performed. The first was admittedly crude but, surprisingly, yielded results which did not disagree appreciably with those of the second and more refined experiment. In both instances, the self-shielding studies were conducted with sodium tungstate, as large quantities of the bronzes were not available.

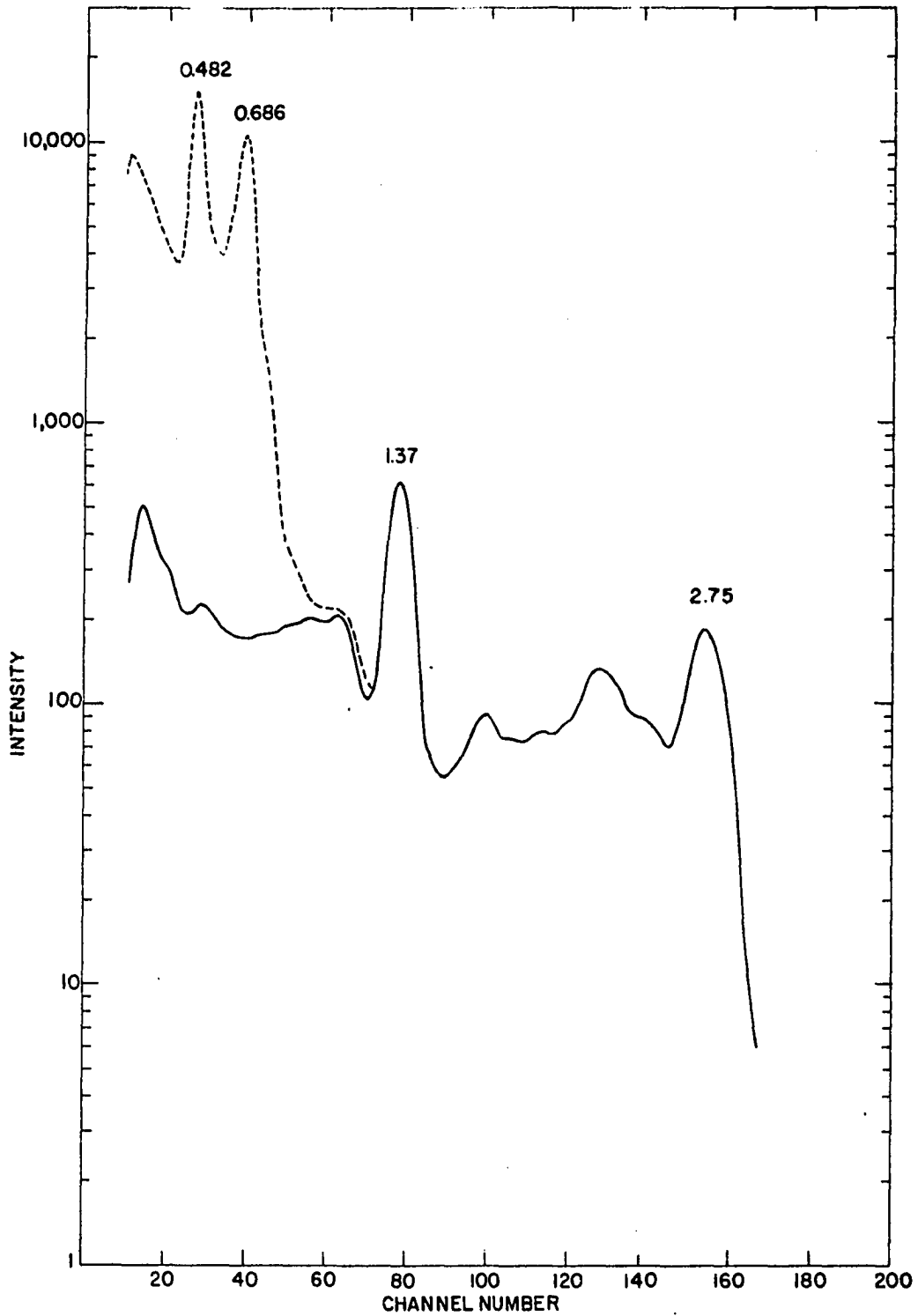


Figure 5. Gamma-ray spectra of neutron activated $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ before and after NOCl separation

In the first experiment, samples of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ varying in weight from 10.6 to 151.7 mg were placed in gelatin capsules and activated in a thermal flux of 8×10^9 neutrons/cm²-sec for 15 minutes. The samples were then reweighed into new gelatin capsules and the gamma-ray spectrum of each sample was accumulated under identical geometry conditions with the RCL pulse height analyzer. The photopeak height of the 1.37 Mev Na^{24} gamma-ray divided by the accumulation live time was taken as a measure of the sodium activity. Any spurious contribution to the photopeak height was taken into consideration by subtraction of the intensity of the high energy trough of the photopeak from the peak height. The activities thus measured were corrected for decay to a common time and were converted to specific activities (counts/min-mg) by dividing by the weight of the sample.

The results, shown in Figure 6, suggested a self-shielding effect which is a linear function of the sample weight. This was probably accidental for, as mentioned above, the conditions of the experiment were not rigidly fixed. Probably the greatest source of error was the sample encapsulation. Among other things, self-shielding is a function of the density of the sample. In this experiment, the volume of the capsules was larger than the sample volumes which prevented control of the shape and density of the sample. The fact that no chemical separation of the W^{187} activity was carried out in this experiment probably does not introduce too great an error. In the case of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, the resolution of the gamma-ray spectrometers available to the investigation was sufficient to almost completely isolate the photopeak of the 1.37 Mev Na^{24}

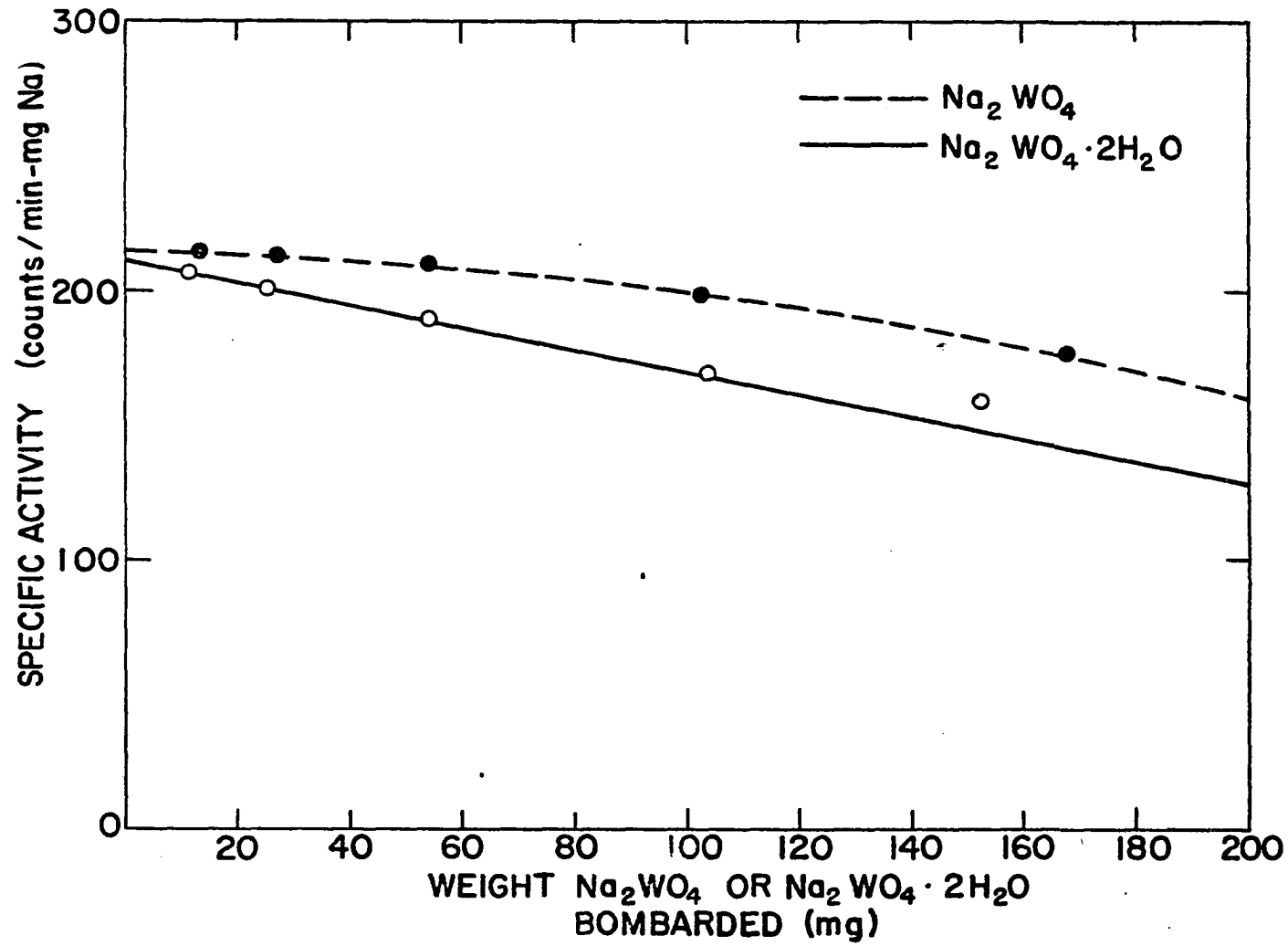


Figure 6. Specific activity versus weight of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ or Na_xWO_3 bombarded

gamma-ray (see Figure 5). This certainly would not be so for a bronze such as N-2-A. Finally, the activities may be somewhat in error in some cases as a result of the difficulty in accurately ascertaining the exact height of the photopeak.

The second experiment represented a considerable refinement of the one described above. The first alteration in the procedure was the use of anhydrous sodium tungstate, Na_2WO_4 , rather than the dihydrate, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. There was some doubt as to the exact hydration number of the "dihydrate". A sample of the dihydrate, when heated at 110°C to constant weight, was found to lose 5% more weight than that calculated on the basis of a hydration number of two. This would have its most serious consequence in the subsequent use of the dihydrate as a standard in the actual activation analysis. Henceforth, when the procedure required the use of sodium tungstate, the anhydrous salt was used. The anhydrous sodium tungstate was not observed to be deliquescent, a sample exposed to the atmosphere for 24 hours gaining only 0.22% in weight. An agate mortar and pestle were used to finely powder the Na_2WO_4 .

The sample containers of this and subsequent experiments were fashioned from one-inch sections of 2mm ID quartz tubing and $1\frac{1}{8}$ -inch sections of undersized 2mm quartz rods. Figure 7 is a sketch of one of these containers, as well as the holder that was used. One end of each rod was fused until a bead was formed that conformed to the ID of the tube. The rods were held in place in the tubes with thin strips of Scotch cellophane tape. The containers were placed in a holder which was constructed from a 2-inch section of 1-inch diameter plexiglass rod. Holes,

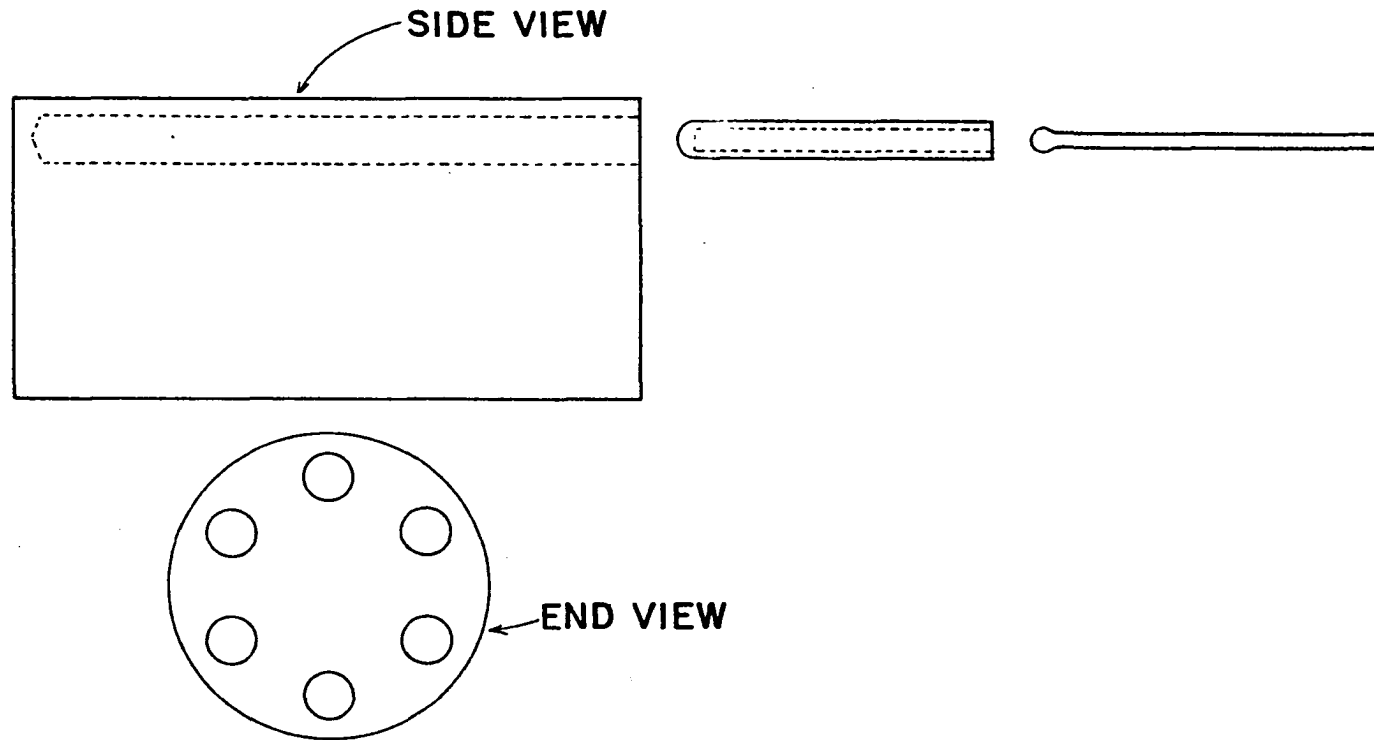


Figure 7. Sample container and holder

which had diameters just large enough to accommodate the sample containers, were drilled about the periphery of the rod. The containers were held in place in the holder by filling the remaining volume of each hole with cotton and sealing the end of the holder with Mylar tape. This holder was positioned in the rabbit between two pieces of Styrofoam to absorb the shock which occurs when the rabbit hits the end of the pneumatic tube.

Five samples of Na_2WO_4 varying in weight from 12.6 to 167.3 mg were activated in a thermal flux of 8×10^{10} neutrons/cm²-sec for three minutes. The samples were then transferred to porcelain boats and heated to 800°C for 1 1/2 hours in an atmosphere of NOCl . The gamma-ray spectrum, accumulated for each with the RCL pulse height analyzer, confirmed a complete radiochemical separation. A GM counter was used to assay the Na^{24} activity. Identical geometry conditions were maintained. At least 10000 counts were recorded for all but the lowest weight NaCl sample. Thus, the statistical counting error was 1% or less. For the lowest weight sample, the error was 1.2%. The lowest weight NaCl sample was removed from the boat, weighed with an Ainsworth microbalance, and returned to a new boat for counting. The others were weighed following the counting procedures. Their weights were determined with a Mettler automatic balance by weighing the boats before and after the removal of the NaCl with water. The activities were corrected for decay and converted to specific activities. The specific activities are shown in Figure 6 plotted versus the weights of Na_2WO_4 samples bombarded in the reactor. The specific activity does not appear to be a linear function of

the sample size as was observed in the first experiment. This non-linear relationship is perhaps in better agreement with the nature of the self-shielding effect. The results of this experiment indicate that the self-shielding effect for a 25 mg Na_2WO_4 sample would be less than 1%.

Isotopic dilution

As a result of the volatilization of the product, NaCl , in the NOCl reaction with Na_xWO_3 and Na_2WO_4 , it was necessary to include the technique of inverse isotopic dilution in the post-irradiation treatment of the sodium tungsten bronzes. A discussion of isotopic dilution methods is given, for example, by Overman and Clark (52). In order to determine the amount y mg of sodium present in the bronze whose specific activity as a result of the irradiation is S_0 counts/min-mg Na, z mg of non-radioactive sodium as Na_2WO_4 (diluant) are added to the bronze and a portion of this isotopic mixture of sodium isolated as NaCl with NOCl . The specific activity of the NaCl is S counts/min-mg Na. Since the total activity remains constant,

$$(y + z)S = yS_0 \quad (10)$$

or, rearranging,

$$y = \frac{1}{S_0/S - 1} z \quad (11)$$

It is seen that only two specific activities and the weight of the diluant need be known to determine the sodium content of the bronze. The sodium content can then be converted to an x value, assuming the tungsten-to-oxygen ratio of the bronze to be 1:3, from the relation,

$$x = 10.084 \left[\frac{Y}{W - Y} \right], \quad (12)$$

where w is the weight of the bronze sample.

The following experiment established the applicability of the isotopic dilution technique to the current problem. Two 50-mg samples of Na_xWO_3 (N-2-A) and a 50-mg Na_2WO_4 sample were activated in quartz tubes for three minutes in a thermal flux of 8×10^{10} neutrons/cm²-sec. These samples were then weighed into porcelain boats. Into the boats containing the Na_xWO_3 , 50 mg inactive Na_2WO_4 was weighed. The boats and contents were exposed to NOCl for 60 minutes at 800°C. Gamma-ray spectra of the NaCl products were accumulated under identical geometry conditions with the RCL pulse height analyzer. The counts in the channels comprising the photopeak of the 1.37 Mev Na^{24} gamma-ray were read-off the digital recorder tape and summed. The sums were corrected for background and divided by the live-time of the accumulation. The resulting activities were corrected for decay and converted to specific activities by dividing by the weights of sodium in the NaCl products. A Mettler balance was used for determining the weight of the NaCl , as well as for all other weighings of this experiment. The boats were weighed before and after the removal of the NaCl with water. The statistical counting errors were less than 1%.

In this manner, all the variables of Equations 11 and 12 were evaluated. The specific activity S_0 was determined from the simultaneously activated Na_2WO_4 sample. The results of this experiment are summarized in Table 3. The observed x values of 0.108 and 0.115 agreed with that of ~ 0.1 which was predicted for this bronze from its method of preparation.

Table 3. Isotopic dilution analysis

w (mg Na _x WO ₃)	z (mg Na)	$\frac{S_0}{S}$ (cpm/mg Na)	y (mg Na)	x
47.2	7.90	3904	0.500	0.108
47.6	7.79	3904	0.535	0.115

Analysis of Na_xWO₃ (N-2-A)

The tetragonal sodium tungsten bronze, N-2-A, with x estimated to be ~0.1, was analyzed according to the NOCl destructive activation method. The size of the bronze samples in all but one instance was 25 mg. If the self-shielding curve shown in Figure 7 is accurate and if its extrapolation to the case of Na_xWO₃ is valid, the self-shielding effect of a 25-mg Na_xWO₃ sample is less than 1%. Nevertheless, the size of the Na₂WO₄ standards was likewise chosen to be 25 mg in all but the one instance. Thus, any self-shielding of the bronze would be compensated by the self-shielding of the standard. The one exception mentioned was an activation of 10-mg bronze samples and a 50-mg Na₂WO₄ standard. The sizes were deliberately chosen in an attempt to observe a self-shielding effect. Presumably, any observed self-shielding could be corrected using Figure 7.

The procedure of the analysis was essentially that which was developed in the preceding experiments and is presented here in outline form.

1. The samples and standards were weighed into 2-mm ID quartz

tubes with a Mettler balance and placed in Lucite holders.

2. Ten bronze samples (and six Na_2WO_4 standards for evaluating S_0) were activated in five bombardments. The thermal flux was 8×10^{10} neutrons/cm²-sec. Bombardments #1 and #2 were of three minutes duration. Bombardments #3, #4, and #5 were of five minutes duration.
3. Following the bombardments, the samples and standards were weighed into porcelain boats. Twenty-five mg inactive Na_2WO_4 (50 mg in the case of bombardment #2) were weighed into the boats containing the bronze samples. All post-irradiation weighings were accomplished with a microbalance.
4. The boats and contents were reacted with NOCl for 75 minutes at 800°C.
5. A gamma-ray spectrum, accumulated with the RCL pulse height analyzer for each NaCl product, confirmed a complete radio-chemical separation.
6. The NaCl products of bombardments #1 and #2 were counted with the GM counter. The NaCl products of bombardments #3, #4, and #5 were counted with the single channel pulse height analyzer which was set to discriminate against all energies (pulses) less than 1.00 Mev. At least 10000 counts were recorded to limit the statistical counting error to 1% or less. Identical geometry conditions were maintained in assaying the activities of any one bombardment. The activities were corrected for background and decay.

7. The NaCl weights were determined by weighing the boats before and after the removal of the NaCl with water. With these weights, the specific activities, S_0 and S , were calculated.
8. Finally, the values were calculated using Equations 11 and 12.

The results of the NOCl destructive neutron activation analysis of the sodium tungsten bronze N-2-A are given in Table 4. \bar{S}_0 represents the average of the specific activities of the standards. The average value of x is 0.0991. The standard deviation of x is ± 0.0056 or 5.6%. The standard deviation of the average value of x is ± 0.0018 or 1.8%. In bombardment #2, the specific activity S_0 was corrected for self-shielding from 50 mg Na_2WO_4 to 10 mg Na_2WO_4 using Figure 7. Had the uncorrected

Table 4. NOCl destructive neutron activation analysis of sodium tungsten bronze N-2-A

Bombardment	w (mg Na_xWO_3)	z (mg Na)	S_0 (cpm/mg Na)	S	y (mg Na)	x
	24.436	3.925	4526	262.1	0.2412	0.1005
	8.852	8.206	3856 ^a	41.01	0.08821	0.1015
	9.519	8.651		42.64	0.09673	0.1035
	25.338	4.715	6736	313.9	0.2304	0.0925
	26.949	4.406		423.1	0.2953	0.1117
	21.739	4.414		302.4	0.2074	0.0971
	24.908	4.022	12165	657.5	0.2298	0.0939
	26.139	3.868		731.3	0.2475	0.0964
	29.099	4.264	11643	721.3	0.2816	0.0985
	24.650	4.059		628.4	0.2315	0.0956
					Average	0.0991

^aCorrected for self-shielding.

value of $S_0 = 3784$ counts/min-mg Na been used, the calculated x values would have been 0.1035 and 0.1056. That these values are in greater discord with the average x value than the corrected values suggests a difference in the self-shielding of Na_xWO_3 and Na_2WO_4 of this bombardment. However, the precision of the analysis does not permit the categorical assertion of the occurrence of self-shielding.

Bromine Trifluoride

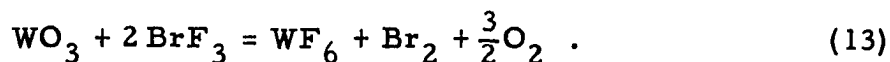
Introduction

The second of the two types of destructive neutron activation analysis of the sodium tungsten bronzes involved the reaction of the bronze with bromine trifluoride.

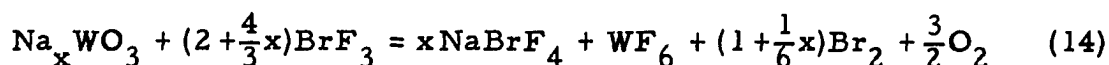
The interhalogen compound bromine trifluoride is a light yellow-green liquid with a normal boiling point of 127.6°C and a freezing point of 8.8°C . This extremely reactive substance is especially valuable as a powerful fluorinating agent, converting many metals and their oxides to fluorides. In many of its reactions with oxides and oxyanions, molecular oxygen is liberated in quantitative yield (53-55). The specific conductivity of bromine trifluoride is $8.0 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C (56). This high electrical conductivity has been attributed to self-ionization to BrF_2^+ and BrF_4^- . In accordance with this proposed mode of self-ionization, bromine trifluoride is a parent solvent for a system of acids such as BrF_2SbF_6 and bases such as KBrF_4 (57).

The reaction of tungsten(VI)oxide with bromine trifluoride has been reported by Hoekstra and Katz (54) to occur readily according to the

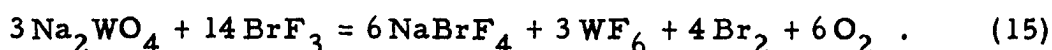
equation,



Although no literature can be cited for the reaction of BrF_3 with $\text{Na}_x \text{WO}_3$ or $\text{Na}_2 \text{WO}_4$, these are suspected to react similarly according to the equations,



and



Tungsten hexafluoride has a normal boiling point of 19.5°C and is therefore easily removed, together with the bromine and oxygen, from the reaction system. The isolated sodium bromofluoride NaBrF_4 is a white solid which decomposes slowly to NaF and BrF_3 (58). Whether the sodium is present as NaF , NaBrF_4 , or a mixture of both following the reaction of $\text{Na}_x \text{WO}_3$ with BrF_3 is inconsequential in the neutron activation analysis of the sodium tungsten bronzes, since in this case it is not necessary to weigh the product.

The bromine trifluoride used in this investigation was obtained from the Matheson Company in a lecture size steel cylinder equipped with a Monel needle valve.

Preliminary investigations

The preliminary investigations of the BrF_3 destructive neutron activation analysis were concerned mainly with providing a suitable system in which to carry out the reaction of the BrF_3 and the bronze. The reactivity of BrF_3 and the radioactivity and volatility of the WF_6 product

were the chief considerations in the design of the reaction system.

A copper vacuum line with Teflon traps and copper plated valves was the first system to be designed and constructed. This system was not satisfactory as it prevented direct observation of the reaction. Direct observation of the reaction was required for it was discovered that the bronzes, particularly the tetragonal bronze, reacted only very slowly with the BrF_3 even at temperatures of 80-90°C. A high activation energy for the reaction or the formation of an inert fluoride surface coating has been proposed in other instances when, from a thermodynamic standpoint, a substance should react with BrF_3 but, in practice, the reaction is not realized (54).

Subsequent reactions involving BrF_3 were conducted in Pyrex systems. Sharpe and Emeléus (58) reported that the loss in weight of a 30-gram quartz reaction vessel exposed to BrF_3 was only 0.01% so long as the apparatus was kept dry to prevent formation of HF. Pyrex is more susceptible to attack by BrF_3 , and the Pyrex reaction vessels of this investigation were visibly etched following prolonged exposure to BrF_3 and its fluoride reaction products. Nevertheless, the extent of the etching was still minor and certainly had no adverse effect on the neutron activation analysis. The original Pyrex vacuum line, which consisted simply of a reaction tube and a cold trap, evolved to the final form which is shown in Figure 8.

The bromine trifluoride was introduced to the system via the transfer tube. About 1 ml of the BrF_3 was removed from the cylinder to a 5 ml glass-stoppered volumetric flask, from which it was measured into the

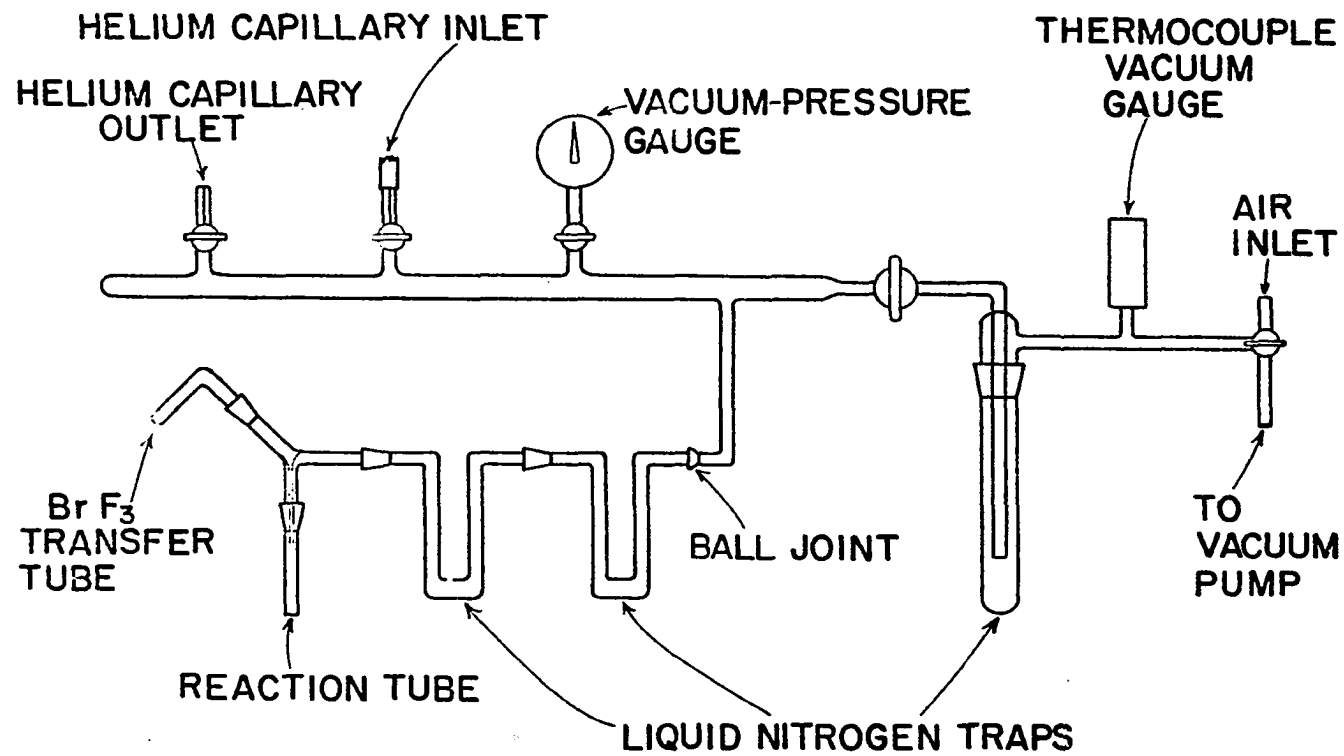


Figure 8. Apparatus used for radiochemical separations involving BrF₃

transfer tubes with a 50 λ micropipet. The reaction tubes of any one bombardment were constructed from the same section of 9mm OD Pyrex tubing in order to normalize the absorption of the gamma radiation in the activity assessment step of the analysis. For the sodium tungsten bronzes, particularly N-2-A, it was necessary to warm the reaction tube to 80-90°C to cause the reaction to go to completion in a reasonable time. Under vacuum conditions, the BrF₃ would distill into the cold traps before completion of the reaction. For this reason, the reactions were conducted at atmospheric pressure under helium. The helium, admitted through the capillary inlet on the manifold, prevented condensation of oxygen in the traps during the course of the reaction. The traps were cooled with liquid nitrogen.

The transfer tubes were designed in such a way that the BrF₃ could be poured-over into the reaction tube containing the Na_xWO₃ or Na₂WO₄. The Na²⁴ activity of the reaction products was to be counted by placing the reaction tube in the well crystal of the single channel pulse height analyzer. It is desirable in such a counting technique to confine the radioactivity as near to the bottom of the well as possible. However, the reaction of BrF₃ with Na₂WO₄ (and some of the finely powdered cubic bronzes) occurs instantaneously and vigorously. Thus, in order to prevent splattering of the activity high on the side of the reaction tubes, the BrF₃ was vacuum distilled into the reaction tube. After helium was bled into the system, the liquid nitrogen was removed from about the reaction tube. The vigor of the reaction was thereby restrained by the slow melting of the BrF₃.

Dow Corning silicone vacuum grease was used as the lubricant for the ground glass joints of the reaction system. Since bromine trifluoride reacts explosively with silicone grease, only the back 1/4 inch of each joint was lubricated, and then with only a thin film of the grease. A vacuum of $5\mu\text{Hg}$ was achieved with a Welch Duo-Seal vacuum pump, Model 1400. The vacuum was metered with a NRC Type 501 thermocouple vacuum gauge. A vacuum-pressure gauge metered the pressure when helium was bled into the vacuum line. When one atmosphere was attained, the helium capillary outlet was opened. Helium was continuously passed into the system during the actual course of the reaction.

Self-shielding

Once again, the question of tungsten shielding sodium in the neutron bombardment of Na_xWO_3 and Na_2WO_4 was investigated. The earlier NOCl investigation indicated that the self-shielding effect of a 25-mg Na_2WO_4 sample was slightly less than 1%. However, the precision of the NOCl method of analysis was inadequate when distinguishing effects of the order of a percent or two. It was suspected that for sample sizes less than 25 mg there would in fact be no self-shielding and that the expected accuracy of the BrF_3 destructive neutron activation analysis would substantiate this.

Five Na_2WO_4 samples, whose weights varied from 2.073 mg to 13.099 mg, were weighed into the usual quartz tubes using the microbalance. The tubes were placed in a Lucite holder and activated in a thermal flux of 8×10^{10} neutrons/cm²-sec for 2 minutes. Following the bombardment, the samples were weighed into the reaction tubes using

the microbalance and treated with BrF_3 according to a procedure which will be outlined in the next section. The gamma-ray spectrum of the radioactivity of the reaction products of each of the samples was accumulated with the RCL pulse height analyzer. The absence of the characteristic photopeaks of W^{187} established the efficacy of the BrF_3 radiochemical separation. The Na^{24} activity was then counted with the reaction tube in the well-crystal of the single channel pulse height analyzer. The analyzer was set to reject all pulses corresponding to energies less than 1.0 Mev. Sufficient counts were recorded in each case to limit the statistical counting error to less than 1%. The activities, corrected for background and decay, were converted to specific activities (counts/min-mg Na) by dividing by the weights of sodium in the Na_2WO_4 samples which were bombarded. These specific activities are plotted in Figure 9 versus the weights of the corresponding Na_2WO_4 samples. The average value and standard deviation of the specific activity are 19816 ± 151 . These results unequivocally demonstrate the absence of a self-shielding effect for Na_2WO_4 samples whose sizes are less than 13 mg.

The self-shielding experiment just described was repeated, substituting Na_xWO_3 (N-2-A) for Na_2WO_4 . Although no study of self-shielding of sodium by tungsten in Na_xWO_3 had been heretofore undertaken, results similar to those represented in Figure 9 were expected.

Five N-2-A samples, whose weights varied from 3.597 to 15.046 mg, were activated for 15 minutes in a thermal flux of 8×10^{10} neutrons/cm²-sec. The post-irradiation treatment of these samples was identical to that described above. The corrected activities were converted to specific

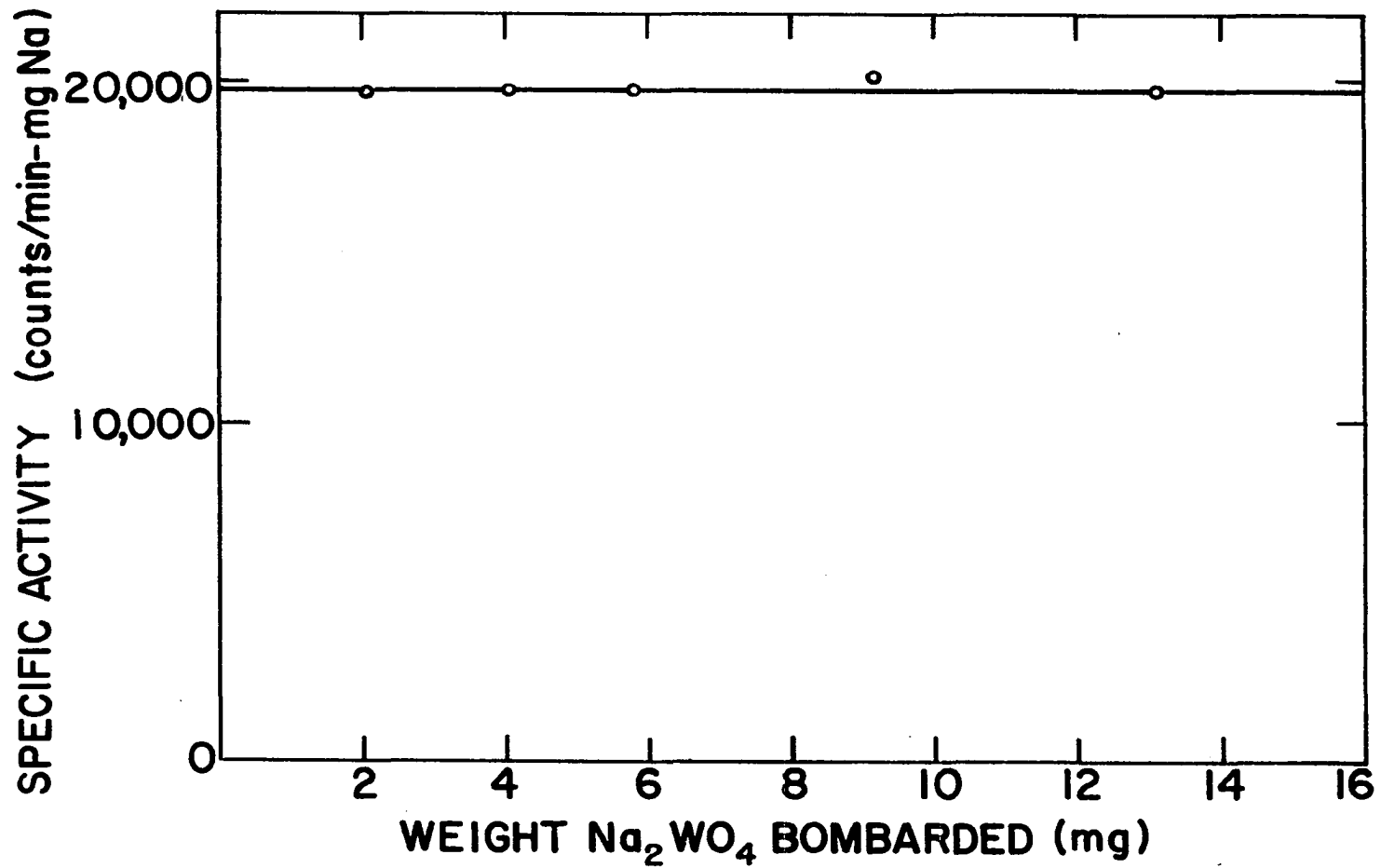


Figure 9. Specific activity versus weight of Na_2WO_4 bombarded

activities (counts/min-mg Na_xWO_3) by dividing by the weights of the samples bombarded. These specific activities are plotted in Figure 10 versus the weights of the corresponding N-2-A samples. The average value and standard deviation of the specific activity are 1296 ± 24 . While the precision was not as great as that obtained in the Na_2WO_4 experiment, the results clearly indicate the absence of a self-shielding effect for Na_xWO_3 (N-2-A) whose sample sizes are less than 15 mg. As the x value of this bronze (~ 0.1) was the lowest of all the bronzes analyzed in this investigation, the results of this experiment were assumed to be valid for all the bronzes studied.

Analysis of Na_xWO_3 (N-2-A)

The tetragonal sodium tungsten bronze N-2-A was analyzed by the BrF_3 destructive neutron activation method in two bombardments of five bronze samples and four Na_2WO_4 standards. The samples and standards were weighed into the usual quartz containers using a Mettler balance, placed in a Lucite holder, and activated in a thermal flux of 8×10^{10} neutrons/cm²-sec. The first bombardment was of 10 minutes duration; the second, of five minutes duration. Following the bombardments, the samples and standards were weighed into the reaction tubes using the microbalance. The weight of each was obtained by the difference in weight of the quartz container determined before and after the transfer of its contents to the reaction tube. The bronze and Na_2WO_4 were then reacted with BrF_3 according to the following procedure:

1. The reaction tube containing either the bronze or the Na_2WO_4 standard was attached to the vacuum line using a thin film of

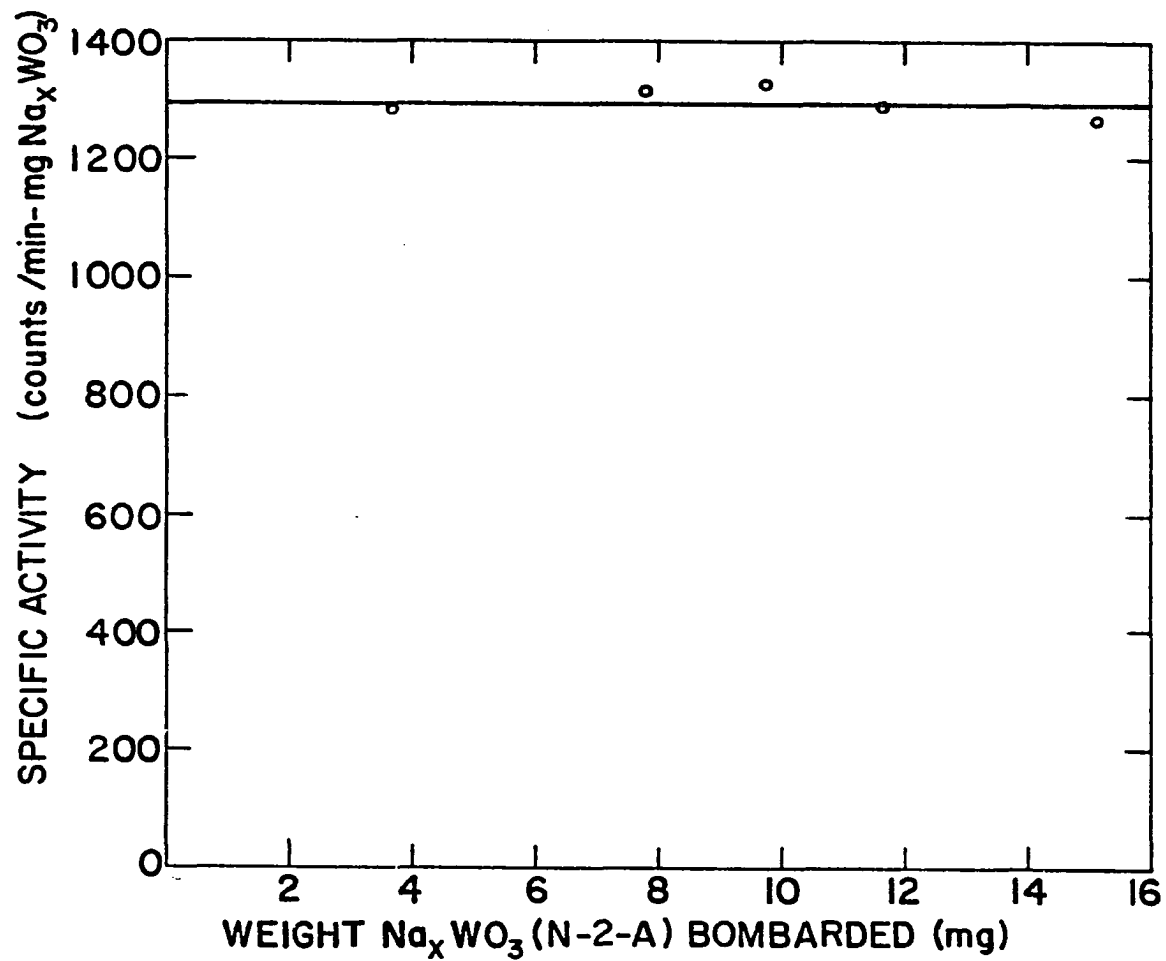


Figure 10. Specific activity versus weight of Na_xWO₃ (N-2-A) bombarded

silicone grease on the remote end of the taper. The line was flushed with helium.

2. The transfer tube, into which was measured 50λ BrF_3 , was attached to the line using silicone grease as above.
3. Liquid nitrogen was placed about the traps and the reaction tube, and the line was evacuated. The BrF_3 distilled into the reaction tube and condensed in a ring about $1\frac{1}{2}$ inches above the bottom of the reaction tube. After helium was re-admitted to the line, the liquid nitrogen was removed from about the reaction tube.
4. As the BrF_3 melted, it reacted with the bronze or Na_2WO_4 standard. It was necessary to warm the reaction tubes containing the bronze samples to $80\text{-}90^\circ\text{C}$ with hot water for 15-20 minutes to effect a complete reaction.
5. The line was then evacuated. The WF_6 , Br_2 , and excess BrF_3 condensed in the U-traps. Pumping on the products in the reaction tube, namely NaBrF_4 and NaF , was continued for 15-20 minutes.
6. Helium was re-admitted to the line and the reaction tube was removed.
7. Another reaction tube containing a sample or standard and a transfer tube containing BrF_3 were attached to the line and steps 3-6 were repeated.
8. When the radiochemical separations were completed, a gas saturation bottle containing a dilute sodium hydroxide solution was attached to the line to the left of the U-traps. The liquid nitrogen

was removed from about the U-traps and the Br_2 and WF_6 were flushed into the gas saturation bottle with helium where they were decomposed. The BrF_3 , which remained in the traps, was removed to the roof for disposal.

Gamma-ray spectra of the radioactivity of the reaction products in the reaction tubes were accumulated with the RCL pulse height analyzer. These spectra confirmed a complete radiochemical separation in each case. The Na^{24} activity was then assayed by placing each reaction tube in the well-crystal of the single channel pulse height analyzer and counting all pulses whose corresponding energies were greater than 1.0 Mev. These activities were corrected for background and decay. The statistical counting error was less than 1%. The activities of the Na_2WO_4 standards were converted to specific activities S_0 by dividing the weights of sodium in the standards. The weight y of sodium in each bronze sample was easily obtained from the relation,

$$y = \frac{A}{S_0} , \quad (16)$$

where A is the Na^{24} activity of the bronze. The x values were then calculated using Equation 12.

The results of the BrF_3 destructive neutron activation analysis of N-2-A are given in Table 5. The average value of x is 0.0986. The standard deviation of x is ± 0.0011 or 1.2%. The standard deviation of the average value of x is ± 0.00049 or 0.50%.

Table 5. BrF_3 destructive neutron activation analysis of sodium tungsten bronze N-2-A

Bombardment	w (mg Na_xWO_3)	A (cpm)	\bar{S}_0 (cpm/mg Na)	y (mg Na)	x
1	5.354	3074	58639	0.05242	0.0997
	4.587	2557		0.04361	0.0968
2	6.755	2638	40293	0.06547	0.0987
	6.146	2392		0.05937	0.0984
	5.861	2305		0.05721	0.0994
				Average	0.0986

NON-DESTRUCTIVE NEUTRON ACTIVATION ANALYSIS

Cadmium-Tungsten Shielding

Introduction

In the neutron energy range extending from 0.4 ev to 1.0 Mev, the total cross section of elements exhibits sharp variations with energy. These variations can be resolved into discrete, sharp peaks or resonances. At these resonance energies, the cross sections are high because the neutron kinetic energy is just that which will form the compound nucleus with an excitation energy equal to one of its energy states. In some instances, the resonance cross sections are extremely high, for example 27600 barns at 1.44 ev for In^{115} . Substances exhibiting such extremely high resonance cross sections can be employed as energy-sensitive neutron filters for isolating the effects of various parts of the reactor neutron spectrum.

The resonance parameters of Na^{23} and W^{186} (49, 59) are listed in Table 6. Considering the high neutron cross section of W^{186} at 18.8 ev, it was thought that the total observed activation of W^{186} contained an appreciable contribution from absorption in this resonance peak and hence might be greatly reduced by shielding the sample with tungsten metal, thereby selectively removing from the flux those neutrons with energies within this peak. At the same time, activation of W^{186} and Na^{23} with thermal neutrons could be prevented by shielding the sample with cadmium. Thus, ideally, only resonance activation of Na^{23} by neutrons within its peak at 2850 ev would be observed. Even if this cadmium-

Table 6. Neutron resonance parameters of Na²³ and W¹⁸⁶

Nuclide	Total cross section at resonance σ_0 (barns)	Resonance energy E_0 (ev)	Width of resonance at half height Γ (ev)
Na ²³	372	2850	405
W ¹⁸⁶	14200	18.8	0.282
W ¹⁸⁶	< 20	175	0.023
W ¹⁸⁶	180	221	0.468

tungsten shield were not entirely effective in preventing activation of W¹⁸⁶, hopefully the W¹⁸⁷/Na²⁴ activity ratio would be reduced to the extent that the Na²⁴ activity could be isolated and assayed by the ordinary techniques of gamma-ray scintillation spectroscopy.

Cadmium ratios of W¹⁸⁶ and Na²³

Prior to the actual activation of Na_xWO₃ or Na₂WO₄ in a cadmium-tungsten shield, the cadmium ratios of W¹⁸⁶ and Na²³ bombarded in the pneumatic tube of the reactor were obtained. If a detector is exposed to the moderated flux of a reactor, essentially it is activated by only thermal and resonance energy neutrons. However, if the detector is covered with cadmium, the cadmium will absorb almost all the neutrons with energies less than 0.4 ev (cadmium cut-off). The large thermal neutron cross section of cadmium is due to a Cd¹¹³ resonance at 0.176 ev of 58000 barns which is wide enough to overlap the thermal region. Thus, the resulting activation of the detector is induced by neutrons with energies greater

than 0.4 ev.

For this case, the cadmium ratio, R_{Cd} , is defined as

$$R_{Cd} = \frac{A_t + A_r}{A_r} = \frac{A_t}{A_r} + 1, \quad (17)$$

where A_t and A_r are the activations due to neutrons of thermal and resonance energies, respectively. Since these activations can be related to the neutron fluxes, the cadmium ratio can be used to obtain a ratio of the thermal to the resonance flux. The cadmium ratio depends not only on the neutron spectrum and, therefore, the position of the detector in the reactor, but also on the nature of the detector since the activation is a function of the variation of the cross section with energy.

The cadmium ratio of W^{186} was measured by activating two 0.5-mil foils of high purity tungsten one of which was wrapped in approximately 30 mil cadmium foil. The tungsten foil was obtained from the H. Cross Company. The foils were simultaneously exposed to the reactor neutron flux for 15 minutes. The reactor was operated at a power of 10 watts (thermal flux = 8×10^7 neutrons/cm²-sec). Following the bombardment, the activity of the foils was counted with a GM counter. The statistical counting errors were less than 1.5%. A cadmium ratio of 4.05 was calculated from the experimental data, which are given in Table 7. This indicates that the resonance response of the tungsten detector is about 1/3 the thermal response, and that the proposed resonance activation might be successful.

The cadmium ratio of Na^{23} was measured by activating two 3-mg samples of NaF in the usual quartz containers. (F^{19} has no interfering

Table 7. Cadmium ratio of W^{186}

Foil	Weight tungsten foil (mg)	Cd foil (mil)	Activity (cpm)	Specific activity (cpm/mg w)
1	29.2		4225	145
2	23.6	30	845	35.8

resonances.) One of the containers was wrapped in approximately 30 mil cadmium foil. The samples were simultaneously exposed to the reactor neutron flux for two minutes. The reactor was operated at a power of 10 kilowatts (thermal flux = 8×10^{10} neutrons/cm²-sec). Following the bombardment, the samples were weighed into 1/2-ml centrifuge tubes using the microbalance. With the centrifuge tube in the 3 1/2-inch by 3 1/2-inch well-crystal, the gamma-ray spectrum of each sample was accumulated with the Nuclear Data pulse height analyzer. All pulses analyzed and stored in channels corresponding to energies greater than 1.24 Mev were summed. Activities were calculated by dividing the summations by the live-time of the accumulations. The statistical counting errors were less than 1%. From the experimental data, which are given in Table 8, a cadmium ratio of 46.6 was calculated for Na^{23} . This indicates that the resonance response of the sodium detector is only about 1/46 the thermal response.

Since the cadmium ratio of Na^{23} is much greater than that of W^{186} , it is clear that a cadmium shield alone would be detrimental to achieving a reduction in the W^{187}/Na^{24} activity ratio of Na_xWO_3 . Thus, for such a

Table 8. Cadmium ratio of Na²³

Sample	Weight NaF (mg)	Cd foil (mil)	Activity (cpm)	Specific activity (cpm/mg Na)
1	3.254		58082	32594
2	3.245	30	1243	699.5

reduction to be realized, it is important that the tungsten shield be effective in removing from the resonance neutron spectrum those neutrons with energies responsible for the resonance activation of W¹⁸⁶. The success of cadmium-tungsten shielding for the non-destructive neutron activation analysis of the sodium tungsten bronzes would depend on the extent to which this selective energy filtration could be achieved.

Shielding experiments

Two shielding experiments were conducted. The first involved activating Na₂WO₄ within a cadmium shield; the second, within a cadmium-tungsten shield. In each bombardment, an unshielded Na₂WO₄ sample was simultaneously activated to assess the effect of the shield upon the W¹⁸⁷/Na²⁴ activity ratio.

For the cadmium shielding experiment, the shield consisted of a small canister which had 30-mil walls and was large enough (about 1/2-inch in length by 1/4-inch in diameter) to just accommodate a No. 5 gelatin capsule. Approximately 50 mg Na₂WO₄ was weighed into such a capsule and placed within the cadmium canister. This sample was exposed, together with an unshielded 50-mg Na₂WO₄ sample, for 30 minutes in the

neutron flux of the reactor operated at a power of 10 kilowatts. After the bombardment, the samples were transferred to new gelatin capsules and their gamma-ray spectra were accumulated with the RCL pulse height analyzer. These spectra are shown in Figure 11 in which the W^{187} contribution to the spectrum of each sample has been normalized. As expected from the results of the cadmium ratio experiments, the W^{187}/Na^{24} activity ratio of the cadmium shielded Na_2WO_4 sample was greater than that of the unshielded Na_2WO_4 sample.

For the cadmium-tungsten shielding experiment, a tungsten shield was constructed which consisted of an aluminum spool about which was wrapped 5 - 10 mil tungsten wire. This shield is shown drawn to scale in Figure 12. The spool, $2 \frac{3}{8}$ inches in length by $\frac{3}{4}$ inch in diameter, was wound with the tungsten wire until the tungsten shell was 30 mil thick. A lathe was used for this purpose. From a $\frac{1}{2}$ -inch tungsten rod, $\frac{1}{32}$ -inch discs were cut and cemented to the two aluminum end-plugs of the spool. Approximately 50 mg Na_2WO_4 was weighed into a gelatin capsule and placed within the tungsten shield. The tungsten shield was in turn placed within a cadmium canister whose walls were 30 mil thick. This assembly, together with an unshielded 50-mg Na_2WO_4 sample, was exposed for 30 minutes in the neutron flux of the reactor operated at a power of 10 kilowatts. After the bombardment, the Na_2WO_4 samples were transferred to new gelatin capsules and their gamma-ray spectra were accumulated with the RCL pulse height analyzer. The spectra of the unshielded Na_2WO_4 samples of both shielding experiments were identical as expected. The spectrum of the cadmium-tungsten shielded

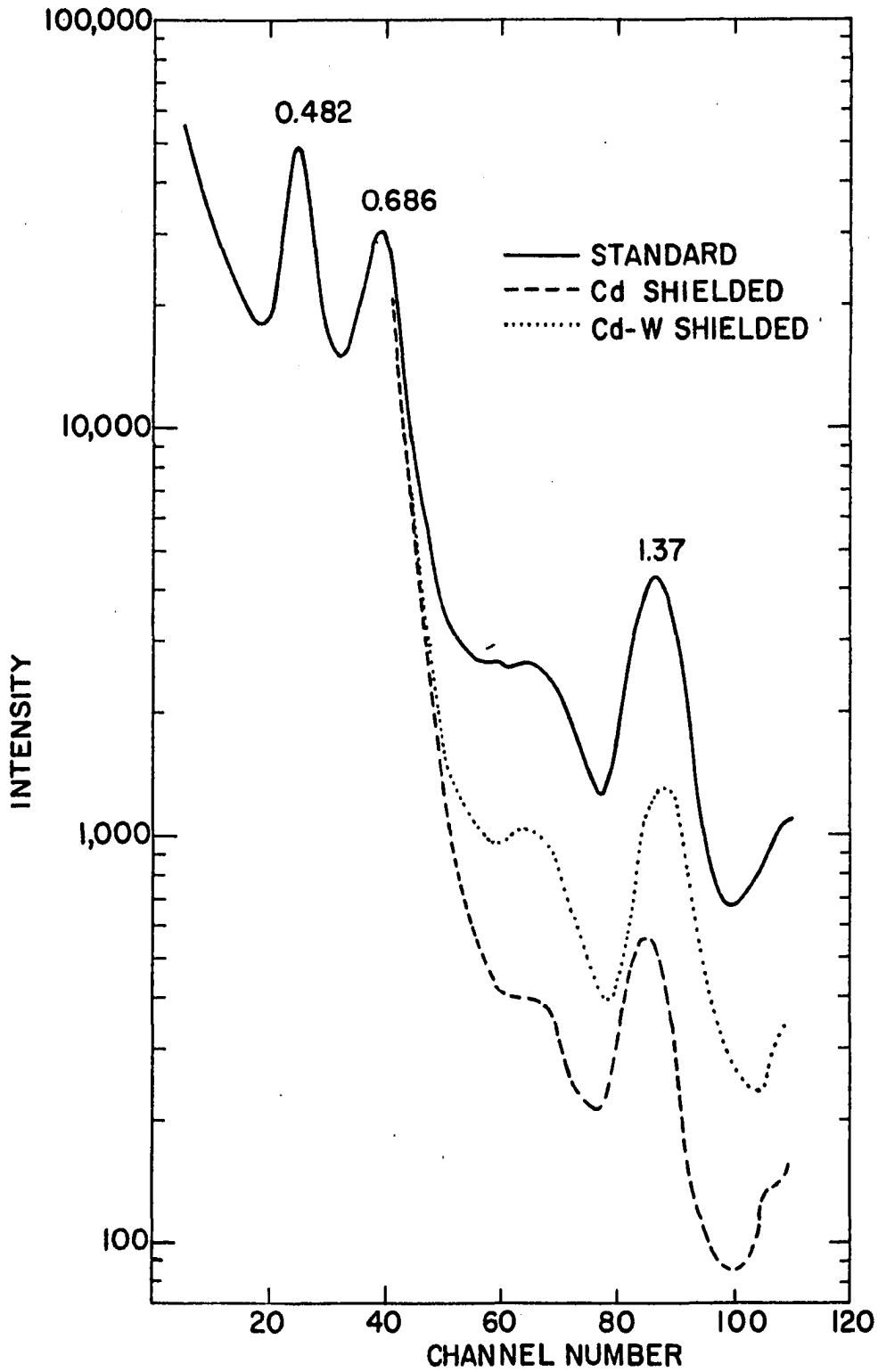


Figure 11. Gamma-ray spectra of neutron activated Na_2WO_4

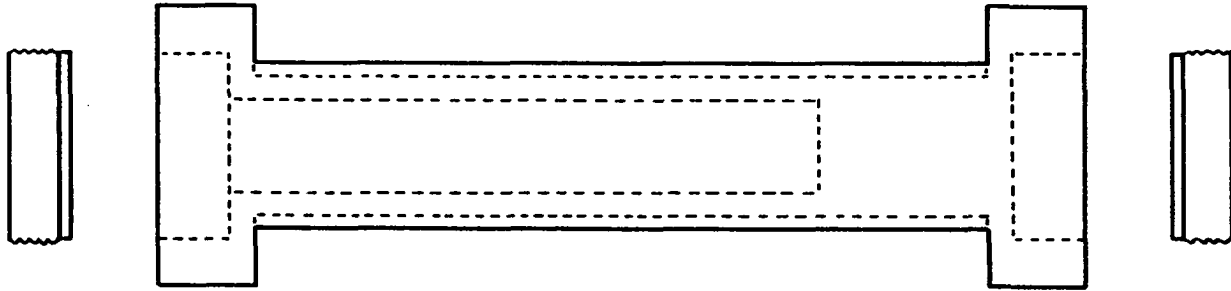


Figure 12. Tungsten shield

Na_2WO_4 is shown in Figure 11 together with the spectra of the cadmium shielding experiment.

It is observed from Figure 11 that the cadmium-tungsten shield effected an enhancement of the $\text{W}^{187}/\text{Na}^{24}$ activity ratio rather than the anticipated reduction. The tungsten shield does reduce the resonance activation of W^{186} somewhat, as evidenced by a comparison of the spectra of the cadmium and cadmium-tungsten shielded Na_2WO_4 samples; but the effect is rather insignificant. Obviously the resonance cross section of tungsten at energies other than 18.8 ev is not sufficiently large that the 30-mil tungsten shield functions effectively as a neutron filter.

Thus, as a consequence of the adverse effect of the cadmium-tungsten shield on the $\text{W}^{187}/\text{Na}^{24}$ activity ratio, isolation of the Na^{24} activity in the activation step of the analysis was not realized.

Spectrum Stripping

Introduction

Another method for isolating the Na^{24} activity without recourse to radiochemical separation is the gamma-ray spectroscopic technique of spectrum stripping. The multi-channel pulse height analyzers of this investigation feature a data complement mode which permits the selective stripping of photopeaks from a composite spectrum. In this mode, the data in each channel of the memory is automatically complemented. By complement it is meant that the count data of a channel represented by a binary number is changed in such a manner that all 1's are changed to 0's and all 0's are changed to 1's. When the data in a channel

representing a number n are complemented, the data represent the number's complement n_c . If additional data representing a number b are accumulated in this channel, the data now represent the sum $(n_c + b)$. If these data are likewise complemented, the data represent the complement of $(n_c + b)$, $(n_c + b)_c$, which is equal to $(n - b)$.

In this way, the photopeaks corresponding to the gamma-rays of W^{187} can be stripped from the composite $Na^{24}-W^{187}$ gamma-ray spectrum. The data in each channel of the $Na^{24}-W^{187}$ spectrum are complemented. A W^{187} source, the intensity of which is judiciously chosen, is used for the data addition to those channels containing the complemented W^{187} data. Obviously, the amplifier gain must remain unchanged if there is to be a correspondence between channel and energy in the two data accumulations. Finally, the data $(n_c + b)$ of each channel are complemented yielding $(n_c + b)_c$ or $(n - b)$. This is equivalent to stripping the W^{187} photopeaks from the composite $Na^{24}-W^{187}$ spectrum.

Analysis of Na_xWO_3 (N-2-A)

The sodium tungsten bronze N-2-A and sodium tungstate were activated, together with 0.5 mil tungsten metal foil, in several bombardments in the reactor. Gamma-ray spectra of the activated N-2-A and Na_2WO_4 were accumulated with the RCL pulse height analyzer. The photopeaks corresponding to the W^{187} gamma-rays were stripped from the $Na^{24}-W^{187}$ spectra of the bronze and standard using the tungsten foil source as described above. If the intensities of the W^{187} activities of the sample, standard, and foil were observed to be essentially equal, the data addition to the complemented data was carried out for the same

live-time as the accumulation of the composite spectrum. If the intensities differed, the data addition was continued just long enough to strip the W^{187} photopeaks from the spectrum, as observed with the cathode ray tube display. The Na^{24} activities were measured from the read-out tape of the stripped spectra by summing the counts in the channels of the photopeak corresponding to the 1.37 Mev gamma-ray and dividing by the live-time of the accumulation. These activities were corrected for background and decay. In only one case did the statistical counting error exceed 1%, and in that case the error was 1.2%. The activities of the standards were converted to specific activities (counts/min-mg Na) and the x values were calculated using Equations 16 and 12.

The x values obtained in this manner which were in best agreement with those obtained in the $NOCl$ and BrF_3 destructive analyses were 0.0935 and 0.0997. The agreement was not always so close. The large deviations that were observed could be attributed to failure to adequately match the W^{187} intensities of the sample, standard, and foil. Differences in the source intensities resulted in an over- or under-subtraction of the W^{187} photopeaks. For large differences in the source intensities, the gain of the linear amplifier of the spectrometer, which is sensitive to changes in source intensity, was effected. Clearly, a difference in gain in the two accumulations seriously detracts from the accuracy of the Na^{24} activity measurement.

It was apparent that the precision required of the neutron activation analysis of the sodium tungsten bronzes could not be easily realized by this spectrum stripping method. Consequently, further investigation in

this direction was discontinued. The ensuing investigation of a precise non-destructive analysis involved a simple coincidence counting technique and energy discrimination.

Energy Summation and Discrimination

Introduction

The two gamma transitions (1.37 and 2.75 Mev) accompanying the decay of Na^{24} are in prompt coincidence. If, following the decay of a particular Na^{24} nucleus, both of the gamma-rays are totally absorbed in a scintillation crystal detector, the light output will represent the sum of the energies of the two gamma-rays, or 4.12 Mev. This is a result of the fact that the interactions of the two gamma-rays, namely photoelectric effect, Compton scattering, and pair production, occur in a much shorter time than the generation and decay of the scintillation. Thus, a peak will appear in the recorded spectrum at 4.12 Mev. At the same time, the photopeaks representing the individual gamma-rays are reduced in intensity. Obviously, placing the Na^{24} source within a large detector increases the probability that both gamma-rays will be totally absorbed in the detector and therefore increases the intensity of the sum peak. In this respect, a well-crystal acts as a simple coincidence counter, the area of the sum peak being a measure of the coincidence counting rate.

Figure 13 shows the Na^{24} gamma-ray spectrum accumulated within and without the 3 1/2-inch by 3 1/2-inch well-crystal. The effect of geometry upon the summation is obvious.

An examination of the decay scheme of W^{187} (49) indicates that no

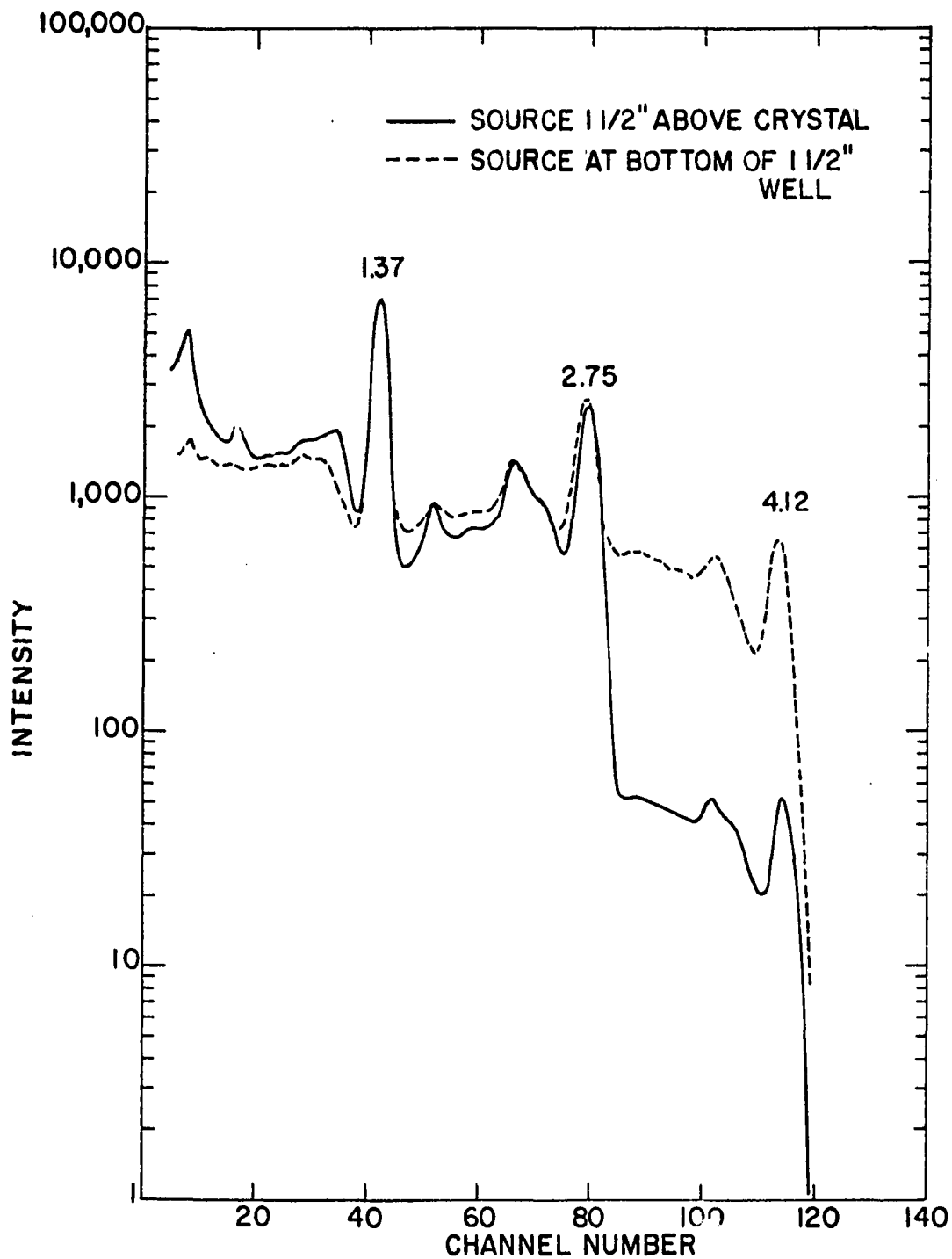


Figure 13. Gamma-ray spectrum of Na^{24} accumulated with the source within and without the 3 1/2-inch by 3 1/2-inch well-crystal

summation is possible beyond 1.000 Mev. Thus, the advantage in using a large well-crystal for the accumulation of the Na^{24} - W^{187} gamma-ray spectrum of an activated Na_xWO_3 or Na_2WO_4 source is to extend the Na^{24} contribution to the spectrum to somewhat beyond 4.12 Mev while the W^{187} contribution remains essentially unchanged (except for a change in the relative intensities of the photopeaks). The gamma-ray spectrum of the activated bronze N-2-A, accumulated both within and without the 3 1/2-inch by 3 1/2-inch well-crystal, is shown in Figure 14, and illustrates the effect of the well in enhancing the separation of the two groups of photopeaks.

Figure 15 shows the gamma-ray spectra, from approximately 1.0 Mev, of Na_xWO_3 (N-2-A), Na_2WO_4 , and NaF which had been activated in the reactor. The spectra were accumulated with the sources in the 3 1/2-inch by 3 1/2-inch well-crystal and are normalized at the 4.12 Mev sum peak. It is observed that beyond channel number 93, there is no W^{187} contribution to the gamma-ray spectrum of the bronze N-2-A. Likewise, beyond channel number 71, there is no W^{187} contribution to the gamma-ray spectrum of Na_2WO_4 . Thus, in assaying the Na^{24} activity, if only the pulses analyzed and stored in channels beyond, for example, channel number 107 (~2.56 Mev) are counted, the isolation of the Na^{24} activity is assured.

Analysis of Na_xWO_3 (N-2-A)

The non-destructive neutron activation analysis of the tetragonal sodium tungsten bronze N-2-A differed from the destructive analyses only in the post-irradiation procedure. The samples and standards were

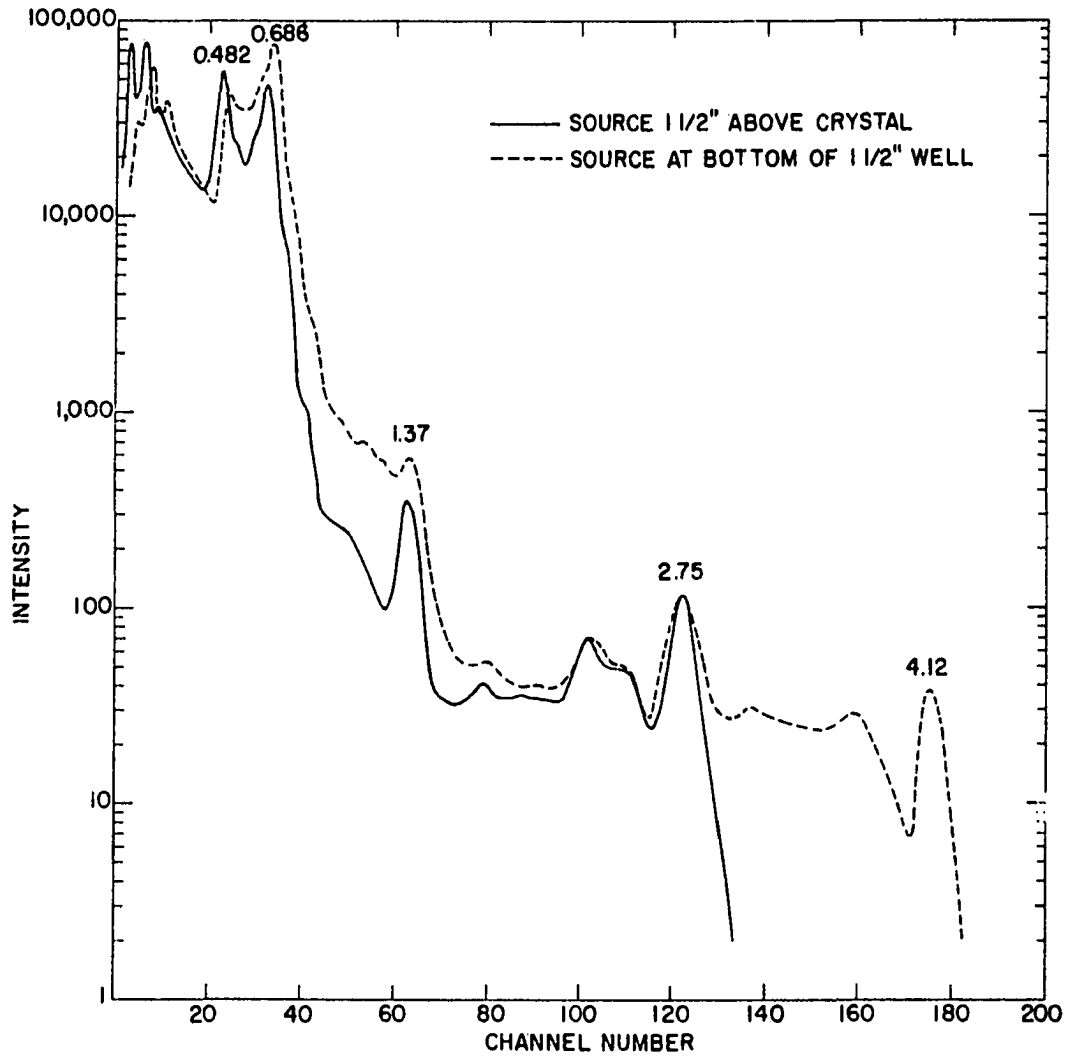


Figure 14. Gamma-ray spectrum of neutron activated Na_2WO_3 (N-2-A) accumulated with the source within and without the 3 1/2-inch by 3 1/2 inch well-crystal

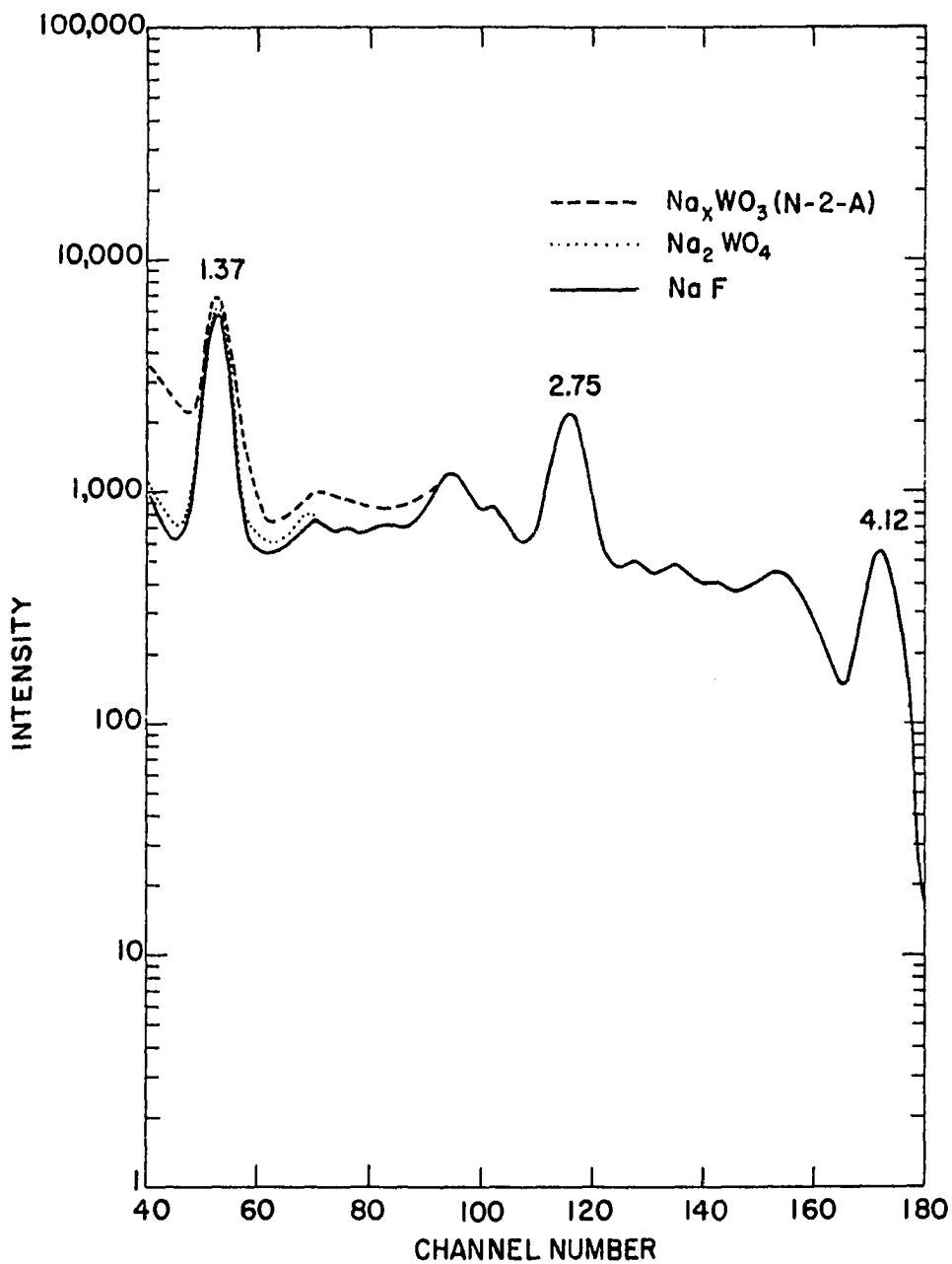


Figure 15. Gamma-ray spectra (from ~ 1.0 Mev) of neutron activated Na_xWO_3 (N-2-A), Na_2WO_4 , and NaF accumulated with the sources within the 3 1/2-inch by 3 1/2-inch well-crystal

weighed into the usual quartz containers with a Mettler balance, placed in the Lucite holder, and activated in a thermal flux of 8×10^{10} neutrons/cm²-sec. Five bombardments, whose duration varied from 2 1/2 to 10 minutes, were made of 13 samples and 15 standards. For two of the bombardments, the standard consisted of 5 - 6 mg Na₂WO₄. For the other three bombardments, 3 - 4 mg NaF was substituted for Na₂WO₄ as the standard. The use of NaF in place of Na₂WO₄ as the standard introduced no problems. At the time when Na₂WO₄ was chosen as the standard, the possibility of self-shielding had not as yet been positively eliminated. The use of Na₂WO₄ as the standard ensured that, if self-shielding was occurring, its effect would be compensated since the sodium in both the sample and standard would be present in roughly the same tungsten environment. However, when subsequent investigations established the absence of a self-shielding effect, it was no longer necessary to restrict the standard to Na₂WO₄. Also, no interference was expected as a result of activation of fluorine. The activation cross section for the reaction $F^{19}(n,\gamma)F^{20}$ is only 0.009 barn and what F^{20} is produced decays to stable Ne^{20} with a 10.7 second half-life.

Following the bombardment, the samples and standards were weighed into 1/2-mil centrifuge tubes using the microbalance. Gamma-ray spectra were accumulated with the Nuclear Data pulse height analyzer with the sample or standard in the 3 1/2-inch by 3 1/2-inch well-crystal. Each gamma-ray spectrum was integrated graphically between the limits 2.56 Mev and 4.43 Mev. This was accomplished by identifying the channels corresponding to the energies 2.56 Mev and 4.43 Mev on the read-out

sheet and summing the counts in the channels between these channel limits. The sum was converted to activity by dividing by the live-time of the accumulation. The activities so determined were corrected for background and decay. The statistical counting error was never greater than 1.3% and in most cases was less than 1%. The activities of the standards were converted to specific activities S_0 by dividing by the weights of sodium in the standards. Finally, the x values were calculated using Equations 16 and 12.

The results of the non-destructive neutron activation analysis of the bronze N-2-A are given in Table 9. The average value of x is 0.0992. The standard deviation of x is ± 0.0032 or 3.2%. The standard deviation of the average value of x is ± 0.00089 or 0.90%.

Table 9. Non-destructive neutron activation analysis of sodium tungsten bronze N-2-A

Bombardment	Standard	w (mg Na _x WO ₃)	A (cpm)	\bar{S}_0 (cpm/mg Na)	y (mg Na)	x
1	NaF	5.375	1659	32136	0.05162	0.0978
		4.365	1287		0.04005	0.0934
2	NaF	3.371	1016.7	31065	0.03273	0.0989
		1.953	595.2		0.01916	0.0999
		2.901	913.6		0.02941	0.1033
3	NaF	2.816	395.1	15308	0.02581	0.0933
		2.455	379.3		0.02478	0.1028
4	Na ₂ WO ₄	5.364	3073	58623	0.05242	0.0995
		5.702	3279		0.05593	0.0999
		5.381	3118		0.05319	0.1007
5	Na ₂ WO ₄	5.828	3216	56081	0.05735	0.1002
		6.295	3369		0.06007	0.0972
		5.093	2873		0.05123	0.1025
					Average	0.0992

NEUTRON ACTIVATION ANALYSIS OF THE CUBIC SODIUM TUNGSTEN BRONZES

Introduction

The sodium tungsten bronzes with x in the range ~ 0.4 to slightly less than 1.0 crystallize in cubic symmetry. For these cubic bronzes, a contraction of the lattice occurs with decreasing sodium concentration. Clearly, if the relationship between the lattice parameter and the sodium concentration x were ascertained, the determination of the x value of the cubic bronzes would be a simple undertaking as the lattice parameters of cubic systems are readily measured using X-ray techniques.

Brown and Banks investigated the conditions under which the starting materials of Equation 4 entered completely into the formation of the bronze. Under the conditions imposed, complete reaction occurred within the range $\text{Na}_{0.30}\text{WO}_3$ to $\text{Na}_{0.85}\text{WO}_3$ as evidenced by the lack of extraneous lines in Debye-Scherrer X-ray powder photographs and, in two instances, by chemical analysis. Thus, it was possible to predict the x value of the cubic bronzes from the ratio of the reactants. These "nominal" x values were plotted versus the lattice parameter a_0 which was precisely determined from the powder photographs. In this manner a linear relation (Equation 6) between the lattice parameter a_0 and the sodium concentration x was obtained by Brown and Banks for the cubic bronzes.

The lattice parameters of the cubic bronzes analyzed in this investigation were precisely determined from Debye-Scherrer powder

photographs as previously described. The x values of these bronzes were then calculated using the Brown and Banks relation. These bronzes, their lattice parameters, and their x values have been listed in Table 2.

Neutron Activation Analysis

The BrF_3 destructive method was chosen for the neutron activation analysis of the cubic sodium tungsten bronzes because it apparently provided the best precision as observed in the analysis of N-2-A. The procedure that was followed was identical to that established for the BrF_3 destructive activation analysis of N-2-A, with the exception that NaF was substituted for Na_2WO_4 as the standard. The use of NaF as the standard greatly reduced the time and effort of the analysis as it eliminated the requirement of radiochemically isolating the Na^{24} activity of the activated standard. Either two or three NaF standards, each weighing approximately 3 mg, were simultaneously activated with each set of bronze samples. The bombardments were of two minutes duration in a thermal flux of 8×10^{10} neutrons/cm²-sec.

The pertinent data and results of the neutron activation analysis of the cubic bronzes are given in Table 10. The standard deviation σ in Table 10 was calculated using the relation,

$$\sigma(\%) = [\sigma_{\text{Na}_x\text{WO}_3}^2 + \sigma_{\text{NaF}}^2]^{1/2}, \quad (18)$$

in which $\sigma_{\text{Na}_x\text{WO}_3}$ and σ_{NaF} are the fractional standard deviations of the specific activity of the bronze (counts/min-mg Na_xWO_3) and of the standard (counts/min-mg Na), respectively.

Table 10. Neutron activation analysis of cubic sodium tungsten bronzes

Bronze	w (mg Na _x WO ₃)	A (cpm)	\bar{S}_0 (cpm/mg Na)	y (mg)	x	\bar{x}	σ
DCL-14-15F	9.738	7158	16968	0.4219	0.4567	0.4620	0.0072 (1.55%)
	9.853	7335		0.4323	0.4628		
	12.961	9465		0.5578	0.4535		
111-A-1	11.776	8624	16597	0.5196	0.4655		
	13.334	9888		0.5958	0.4716		
124-A-6	11.179	11334	19960	0.5678	0.5396	0.5326	0.0091 (1.71%)
	8.341	8302		0.4159	0.5292		
	9.668	9617		0.4818	0.5289		
138-A-1	9.500	10540	20941	0.5033	0.5641	0.5608	0.0044 (0.78%)
	9.724	10761		0.5139	0.5627		
	12.086	13217		0.6312	0.5556		
184-A-1	6.533	9419	21034	0.4478	0.7421	0.7148	0.0287 (4.02%)
	4.972	6944		0.3301	0.7171		
	4.127	5524		0.2626	0.6853		
116-A-4	5.325	7147	21026	0.3399	0.6875	0.6844	0.0077 (1.12%)
	7.332	9825		0.4673	0.6864		
	8.104	10754		0.5115	0.6794		
125-A-2	9.943	15101	21286	0.7094	0.7747	0.7793	0.0058 (0.74%)
	9.762	14878		0.6990	0.7778		
	6.405	9851		0.4628	0.7854		
	4.226	6318	19415	0.3254	0.8411	0.8444	0.0141 (1.67%)
	3.579	5381		0.2772	0.8466		
	6.102	9166		0.4721	0.8455		

Comparison of Activation and X-ray Analyses

The bronze designated DCL-14-15F was obtained from A. Wold of the Lincoln Laboratory of Massachusetts Institute of Technology. Wold determined the x value of this bronze in two ways. The first was the now familiar deduction from the lattice parameter. A lattice parameter of 3.8215\AA was quoted from which an x value of 0.451 was calculated. In the second analysis the bronze was heated in air to 800°C and the weight-gain related to the sodium concentration giving an x value of 0.456. Although no indication of the precision of these results was given by Wold, he expressed uncertainty in the significance of the last figure of his lattice parameter which would be reflected in the third figure of the x value.

The x value of the bronze DCL-14-15F determined by neutron activation analysis was 0.462 ± 0.007 . The x value obtained from the weight-gain analysis is within the standard deviation of the x value obtained by activation analysis; but the x value determined by deduction from the lattice parameter is outside this standard deviation. In view of the uncertainty in the third figure of the x value calculated with the lattice parameter 3.8215\AA , the lattice parameter was re-measured and found to be $3.8225\pm 0.0002\text{\AA}$. This parameter yields an x of 0.463 ± 0.003 which is in excellent agreement with the activation analysis value.

The x values of the cubic bronzes analyzed in this investigation both by the activation method and by the x-ray powder method are presented in Table 11.

The lattice parameter a_0 is plotted versus the x value obtained by activation analysis in Figure 16. A straight line was fitted to these data

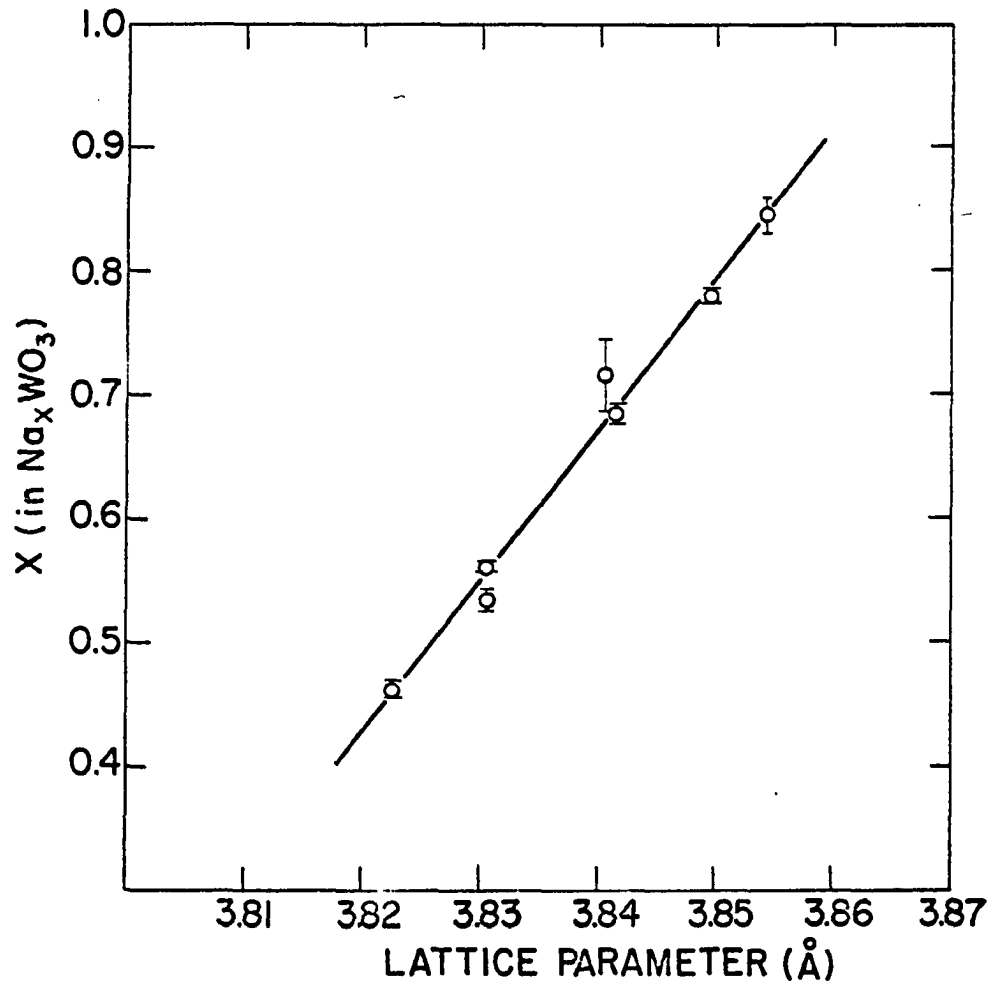


Figure 16. Lattice parameter versus x value obtained by activation analysis for cubic sodium tungsten bronzes

Table 11. Comparison of X-ray and activation analyses of cubic sodium tungsten bronzes

Bronze	x (X-ray) ^a	x (activation)
DCL-14-15F	0.463	0.462
111-A-1	0.562	0.533
124-A-6	0.561	0.561
138-A-1	0.683	0.715
184-A-1	0.694	0.684
116-A-4	0.793	0.779
125-A-2	0.851	0.844

^aCalculated using the relation of Brown and Banks (29).

by the method of least squares. This line is represented by the relation,

$$a_o(\text{\AA}) = 0.0818x + 3.7850, \quad (19)$$

which is in excellent agreement with the Brown and Banks relation,

$$a_o(\text{\AA}) = 0.0819x + 3.7846. \quad (6)$$

The average deviation of x from the least squares line is ± 0.0126 which, in the range of x studied, amounts to 1.5 to 2.7%.

SUMMARY

Analyses and Results

The main obstacle to the neutron activation analysis of the sodium tungsten bronzes was the large W^{187} activity which was simultaneously produced with the Na^{24} activity. This large W^{187} activity prevented accurate counting of the Na^{24} activity, the essential step of the analysis.

The investigation of destructive methods of neutron activation analysis, in which the two activities are radiochemically separated, was complicated by the extreme inertness of the bronzes. Nevertheless, two procedures were established. The first included a high temperature reaction of the bronze with nitrosyl chloride and required inverse isotopic dilution. The second procedure utilized bromine trifluoride to effect the removal of the W^{187} interference.

In the search for a non-destructive method of activation analysis of the bronzes, three techniques were investigated. One, which utilized a cadmium-tungsten shield for the selective activation of Na^{23} , proved to be unsuccessful. Another, which involved stripping the W^{187} contribution from the composite Na^{24} - W^{187} gamma-ray spectrum of the bronze, did not provide the desired precision. The precision of the third technique, however, compared favorably with that of the destructive activation analyses. This method featured a discriminative analysis of the Na^{24} - W^{187} gamma-ray spectra which were accumulated using a well-type detector.

The results of the neutron activation analysis of the tetragonal

sodium tungsten bronze N-2-A are summarized in Table 12.

Table 12. Summary of results of neutron activation analysis of sodium tungsten bronze N-2-A

Method of analysis	\bar{x}	Standard deviation of average value
destructive - NOCl	0.0991	0.0018
destructive - BrF ₃	0.0986	0.0005
non-destructive	0.0992	0.0009

The accuracy of the neutron activation analysis of the sodium tungsten bronzes was established by analyzing cubic bronzes for which the x values were accurately and precisely known from x-ray measurements of their lattice parameters. Seven bronzes with x values from 0.463 to 0.851 were analyzed by the BrF₃ destructive method. In all but one of the analyses, the standard deviation of x was not greater than 1.7%. When the x values of these cubic bronzes, as determined by activation analysis, were plotted versus their corresponding lattice parameters, a linear relationship was obtained which was in excellent agreement with that of Brown and Banks. The average deviation of x from the linear relation was ± 0.0126 which, in the range of x studied, amounts to a 1.5 to 2.7% deviation.

Significance

The neutron activation analysis of the sodium tungsten bronzes is significant in that it provides an accurate method for determining the

sodium concentration of the bronzes regardless of their structure. Here-
tofore, most investigations of the physical properties of the sodium tung-
sten bronzes have been restricted to that range of x in which the bronzes
crystallize in cubic symmetry; for in this range, the x value can be ac-
curately determined from x-ray powder photographs. However, in the
non-cubic range (x less than about 0.4), it has not been possible to de-
termine x with sufficient accuracy to establish a relationship between the
lattice contraction and the x value. Although interesting physical phenom-
ena have been observed and are anticipated in this non-cubic range of the
bronzes, their interpretation in terms of the sodium concentration has
not as yet been possible.

This investigation has shown that neutron activation analysis does,
in fact, provide a suitable method for determining the sodium concentra-
tion of the non-cubic bronzes either directly or, indirectly, if a relation-
ship between the lattice contraction and the x value can now be obtained.

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