TRACE CHARACTERIZATION OF REFRACTORY METALS BY ACTIVATION TECHNIQUES

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Abstract - The application of activation techniques to the assay of the refractory metals niobium, molybdenum, tantalum and tungsten for their trace element impurities is reviewed. Activation with reactor neutrons, fast neutrons, charged particles and photons in connection with both the non-destructive and the radiochemical performance is considered. The decisive contribution of activation techniques to the advances achieved in trace characterization of refractory metals is discussed.

INTRODUCTION

The refractory metals niobium, molybdenum, tantalum and tungsten have several special properties enabling their extensive application in various scientific and technological fields.

In addition to a great number of conventional application in different areas such as lighting industry, chemical engineering, metallurgical processing, high temperature furnace construction etc., recently, new and very special applications are of increasing significance. For example, in the case of niobium, in the center of interest is its superconductivity. Among the transition elements, niobium has the maximum transition temperature (9.5 K) and it is the basic component of almost all technologically interesting superconductors (Nb-Ti, Nb_3Sn, Nb_3Ge). Superconductors and superconductive magnets are of principal importance for new developments in high energy physics, fusion research, energy storage, power transmission and in other fields. High purity niobium is used in the integrated circuits containing Josephson junctions as active elements enabling a new break-through into extremely small dimensions in electronics, and as neutron monitor in nuclear reactors. Niobium and molybdenum are discussed as suitable materials for the first wall in fusion reactors. Many of the properties relevant for the mentioned applications as well as many other properties of refractory metals are strongly affected by trace impurities. Consequently, the trace analytical characterization of refractory metals is very important. The knowledge of the content of impurities is in many instances absolutely necessary for the actual investigation or for the given application.

However, for several reasons, the assay of these metals for trace impurities is a difficult analytical task, especially if they are of high purity. As the activation analysis offers some unique advantages [1], it has become very important in this field.

This review article briefly describes the principles and the characteristic features of activation analysis and discusses the application of the different activation techniques, i.e., neutron activation analysis (NAA), charged particle activation analysis (CPAA) and photon activation analysis (PAA), to trace characterization of refractory metals.

ACTIVATION ANALYSIS TECHNIQUES

Activation analysis [1-4] can be performed (1) instrumentally (sample is directly counted after the irradiation) and (2) radiochemically (prior to coun-

ting, group or individual radiochemical separations are carried out). The principal processes determining the efficiency of an activation technique include the irradiation of the sample in nuclear reactor or an accelerator, gamma-spectrometric measurement and/or radiochemical separation.

Activation

The activation techniques suitable for trace analysis are summarized in Table 1 along with their most important performance data. For the activation, the type of projectile, the energy and the flux (beam) are of fundamental importance. The first two factors determine the type of the analytical reaction and by this fact also the sensitivity as well as the kind and extent of nuclear interferences. In addition, the sensitivity is proportional to the projectile flux (beam intensity).

Table 1. Survey of different activation techniques

Projectiles and source	Mode of projectile production	Projectile energy	Typical analytical reaction	Projectile flux $[cm^{-2}s^{-1}]$
Neutrons				
Nuclear reactor	fission	fission spectrum	(n,γ)	high, 10^{12} – 10^{15}
Neutron generator	$^3T(d,n)^4He$	14 MeV	(n,p), (n,α) $(n,2n)$	medium, 10^8 – 10^{10}
Cyclotron	$d+Be\rightarrow n$	variable spectrum	(n,p), (n,α) $(n,2n)$	high, 10^{10} – 10^{12}
Charged particles $T = p,d,^3He,\alpha$				
Cyclotron, linear accelerator	acceleration	variable	(T,n), $(T,2n)$ (T,p), (T,α)	high, 10^{13} – 10^{14} a)
Photons				
Electron accelerator	bremsstrahlung production	variable spectrum	(γ,n), (γ,p)	high, 10^{13}

a) Number of particles per second; beam intensity = 1 µA = 6.2×10^{12} singly charged particles per second

Among the activation techniques, activation analysis with reactor neutrons remains the most important and the most common [5]. The nuclear reactor can produce fission neutron fluxes between 10^{12} to 10^{15} n $cm^{-2}s^{-1}$, depending on the reactor design. The activation analysis is based on the (n,γ) reactions which are induced by thermal neutrons ($E_n < 0.2$ eV) and by epithermal neutrons ($E_n = 0.2$ eV to 0.5 MeV), whereas the threshold reactions of (n,p) and (n,α) induced by fast neutrons must be considered as possible primary interfering reactions. The thermal activation cross-section σ_{th}, which, together with projectile flux and irradiation time, strongly affects the sensitivity, ranges for the most stable nuclides of the natural elements from 10^{-2} to 10^3 barns. They are, in general, many orders of magnitude greater than the cross-sections for the primary interference reactions which can then occur only to a small extent. However, if the cross section of neutron capture reactions induced on the matrix constituents is very high, the attenuation of the neutron flux in the sample must be considered.

Activation analysis with reactor neutrons is characterized by extremely high sensitivity for a large number of elements. Table 2 provides an impression

of the limits of detection achievable, using the assumed experimental conditions.

Table 2. Limits of detection for activation analysis
with reactor neutrons [a]

Detection limit, g	Element
$10^{-16} - 10^{-15}$	Eu
$10^{-15} - 10^{-14}$	In, Dy
$10^{-14} - 10^{-13}$	Mn, Sm, Ho, Lu, Re, Ir, Au
$10^{-13} - 10^{-12}$	Na, Ar, V, Co, Cu, Ga, As, Br, Kr, Rh, Pd, Ag, I, Cs, La, Pr, Yb, W
$10^{-12} - 10^{-11}$	Al, Cl, K, Sc, Ge, Se, Y, Sb, Xe, Ba, Gd, Tb, Er, Tm, Pt, Os, Hf, Hg, Th, U
$10^{-11} - 10^{-10}$	Si, P, Cr, Ni, Zn, Sr, Nb, Ru, Cd, Sn, Te, Ce, Nd, Ta
$10^{-10} - 10^{-9}$	F, Ne, Mg, Ti, Rb, Mo, Tl, Bi
$10^{-9} - 10^{-8}$	S, Ca, Zr, Pb
$10^{-8} - 10^{-7}$	Fe

a) Assumptions:
activity for detection of indicator radionuclide:
0.1 nCi for $t_{1/2} > 30$ min; 0.5 nCi for 1 min $< t_{1/2} < 30$ min; 1.0 nCi
for 1 s $< t_{1/2} < 1$ min;

thermal neutron flux = 5×10^{13} n cm^{-2}s^{-1}, epithermal flux = 10^{12} n cm^{-2}s^{-1}
irradiation time = 24 h

For the assay of several trace elements, where activation via (n,γ) reactions is not favourable, activation analysis based on threshold reactions of the (n,p), (n,α), and (n,2n) types can be the technique of choice.

The most common source of fast neutrons is still the 14-MeV neutron generator [6] in which neutrons are produced by bombardment of a ^{3}H-target with deuterons accelerated to energies of 50 to 600 keV. The commercially available generators provide effective neutron fluxes in the irradiation position of the order of 10^9 n cm^{-2}s^{-1}. Although recently, generators with higher output have become available providing effective fluxes up to $6 \cdot 10^{10}$ n cm^{-2}s^{-1} [7], these are still not high enough for elemental trace analysis at extremely low level. Additional limitations of this activation technique are caused by the fixed 14-MeV neutron energy being unfavorable for many elements and by limited operating life time of the tritium target.

In recent years, promising progress has been made in activation analysis with fast neutrons produced by bombardment of a beryllium target with energy-rich deuterons [8,9]. In the irradiation position, fluxes higher than 10^{12} are attainable and it is possible to choose the optimum neutron spectrum with respect to sensitivity and interfering reactions in each particular case.

Although charged particle activation analysis (CPAA) is considered as a complementary technique to neutron activation, it offers unique possibilities for solving difficult and special problems in trace element analysis [1,10-12] stemming from its unusual features. One of them is its exceptional universa-

lity. A number of nuclear reactions can be induced on each target nuclide, depending on the kind and energy of the projectile particle (Figure 1), yielding different radionuclides. In fact, for each element at least one sensitive reaction yielding an indicator radionuclide with suitable nuclear properties can be chosen. Another advantage of charged particle activation is the energy variability of the projectiles.

	$-N$ ←	ΔN	→ $+N$	
$-Z$ ↑	$(\alpha,4n)$ $(^3He,3n)$	$(\alpha,3n)$ $(^3He,2n)$	$(\alpha,2n)$ $(^3He,n)$	(α,n)	
ΔZ	$(p,2n)$ $(d,3n)$ $(^3He,p3n)$	(p,n) $(d,2n)$ $(^3He,p2n)$	(d,n) $(^3He,pn)$ $(\alpha,p2n)$	$(^3He,p)$ (α,pn)	(α,p)
	$(^3He,an)$ $(p,p2n)$ $(d,p3n)$	$(^3He,\alpha)$ (p,pn) $(d,p2n)$	Target nuclide	(d,p)	
$+Z$ ↓	(p,α) $(d,\alpha n)$	(d,α) $(p,2pn)$	$(d,2np)$ $(p,2p)$	$(d,2p)$	

Figure 1.   Survey of possible transmutation modes of the target nucleus by charged-particle induced nuclear reactions

Table 3. Detection limits of CPAA considering the "best reaction" on each element

Detection limit	Elements	
$\lesssim 1$ ppb	B, C, N, O, Ca, Y, Pr, Gd	(8)
1 - 10 ppb	Li, Ti, Cr, Co, Ni, Cu, Zn, Ga, Ge, Br, Rb, Zr, Ru, Cd, Sn, Te, Ba, La, Ce, Eu, Ho, Er, Yb, Lu, Hf, W, Os, Ir, Pt, Tl, Pb, Bi	(33)
10 - 100 ppb	H, He, F, Na, Mg, Al, Si, P, S, V, Fe, As, Se, Sr, Nb, Rh, Pd, Ag, Sb, I, Cs, Dy, Au, Hg	(23)
0.1 - 1 ppm	Be, Cl, Mn, In, Re	(5)
>1 ppm	K, Ta	(2)

Light particles, i.e., protons, deuterons, ^{3}He- and α-particles are common projectiles in CPAA. The most suitable source of charged particles for activation analysis is, by far, the cyclotron. The recently developed compact cyclotrons are particulary attractive as they are small and relatively cheap machines, simple to operate, and provide variable energies and high intensities (upto 50-100 µA) of the external beam.

Table 3 surveys limits of detection which have been reported for all particle
types used in CPAA [1,11,12]. As the methodology of CPAA is still in develop-
ment, the limits of detection given in the Table can, in many cases, be further
improved.

CPAA has, however, also some special problems caused mainly by the intense
losses of particle energy in the sample. The consequences of this effect are:
(1) The volume of the sample actually activated is rather small. For this
reason, it is of principal importance to consider how far the activated frac-
tion is representative for the investigated material. (2) Standardization is
more complicated than in neutron activation as sample and standard must be
irradiated separately. (3) The particle energy losses result in the produc-
tion of a large amount of heat. This necessitates efficient cooling of the
sample during the irradiation. Even then, beam intensities higher than about
10 μA can rarely be used and the possible losses of the volatile elements
should not be underestimated.

Photon activation [13-15], usually based on nuclear reactions of (γ,n) and
(γ,p) type, is a useful complement of the neutron and charged particle acti-
vation. The commonly used electron accelerator for photon activation analysis
is the Linac providing electron beam currents upto about 100 μA with desired
energies (up to 35 MeV). Photon activation analysis has been mostly applied
to the determination of light elements, especially carbon, nitrogen and
oxygen.

Counting techniques

Gamma-ray spectrometry [16-18] using semiconductor detectors is essential for
the instrumental   approach of activation analysis or radiochemical approach
mance involving group separations. Gamma-rays with energies higher than 100-
150 keV are normally counted with a lithium-drifted germanium detector. Large
detectors of this type have recently become available having an efficiency more
than 30% as compared with that of a 3"x3" NaI(Tl) detector and an energy reso-
lution down to 1.7 keV (FWHM) for 1.33 MeV photon energy, and a peak-to-comp-
ton ratio better than 50:1. For the detection of γ-rays in the energy
interval 30-150 keV, small intrinsic or planar lithium-drifted germanium detec-
detectors are used, While for γ-rays with energies below 30 keV   Si(Li)
ted silicon detectors. With these special detectors, excellent energy resolu-
tion (as small as 145 eV at 5.9 keV) can be achieved.

Modern gamma-ray spectrometer systems use circuits including a FET preampli-
fier followed by a linear amplifier with a pole-zero control, a pile-up re-
jector, and a baseline restorer. At counting rates up to ca. 10^4 cps, using
the above mentioned system, the energy resolution is determined by the detec-
tor. For low energy photon spectrometry, preamplifiers with pulsed optical
feedback are used. Recently, an electronic circuit for gamma-ray spectrometry
has been developed [19] providing high quality spectra even up to as high coun-
ting rates as $3 \cdot 10^5$ cps. Computer-controlled multichannel analysers have be-
come indispensable for the measurement and evaluation of gamma-ray spectra. A
large number of programs and evaluation procedures have been developed to
computerize activation analysis [20].

The performance of gamma-ray spectrometry can significantly be improved by using
special techniques, such as coincidence and anticoincidence counting arrange-
ments [1]. For example, with a modern anticoincidence set-up consisting of a
Ge(Li) and a large volume NaI(Tl) in an asymmetric arrangement, the Compton
background can be suppressed by a factor of up to 20 in the low-energy region,
with no loss with regard to peak intensities.

When an indicator radionuclide is selectively separated from the radionuclide
mixture, it can be counted with a detector having low or no energy resolu-
tion but a high counting efficiency, e.g., with a NaI(Tl) well type scintilla-
tion counter (γ-rays) or with a Geiger-Müller counter (β-rays). In this way,
the best sensitivities and limits of detection can be obtained in activation
analysis.

Characteristic features of activation techniques

Among the analytical techniques for the determination of trace contents of
elements, activation analysis not only takes an important position but it makes
the ultimate contribution in this field [1,21], especially if extremely
low levels are considered (< ppm).

The principal advantage of activation analysis over all other techniques is complete freedom from blank   in analysing compact solids, such as refractory metals, even when radiochemical separations are used. Also, surface contaminations, involved before and during the irradiation, can be removed by appropriate etching of the sample after the irradiation. Not only contaminations are impossible in the post-irradiation procedures, but inactive carriers are added (0.1-5 mg) to facilitate the performance of radiochemical procedures. Meanwhile, it is well known that the blank determines the limit of detection and is also the main factor affecting the accuracy of each non-activation method involving wet chemical procedures. As no other trace analytical method provides freedom from blank , activation analysis offers the best possibilities for obtaining accurate results, even at extremely low contents.

Another important feature of activation analysis is its high sensitivity. For many elements, it is the most sensitive method available (see Tables 2 and 3). At the same time, activation analysis offers a high degree of selectivity as the radionuclides produced in an activation can be identified according to two characteristic properties: the energy of the gamma-rays (or X-rays) and the half-life. The possibility to irradiate simultaneously the sample and the standard favours good accuracy and precision.

The multielement character and the feasibility of non-destructive analysis (in general, applicable to content > 0.1 ppm) should also be mentioned on the sunny side of the activation techniques.

But the activation techniques, similar to any other, are not free of disadvantages and limitations. The dependance on the expensive irradiation facilities is probably the main limitation. But the necessity of handling radioactive materials also complicates the experimental work. On the other hand, the costs are not so prohibitive as often expressed: the activation analysis can be the cheapest or the most expensive technique, depending on the problem to be solved, and on the irradiation facility used.

        APPLICATION OF ACTIVATION TECHNIQUES TO
        ANALYSIS OF REFRACTORY METALS

The scopes of the individual activation techniques in trace characterization of refractory metals are surveyed in Table 4.

Activation analysis with reactor neutrons
From Table 5 it can be seen that among the refractory metals, only niobium is a convenient matrix for instrumental NAA. After cooling for about 2 hours, necessary for the decay of ^{94m}Nb ($T_{\frac{1}{2}}$=6.26 min), the sample can be counted using a γ-ray spectrometer. Our experience of analyses of niobium samples of different origin and purity grade shows that, in the most cases, only Ta and W can be determined instrumentally in spite of using sophisticated equipment including anticoincidence γ-ray spectrometer. This is caused by several reasons: (1) of all impurities, these two elements are normally present at the highest content in niobium (2) the corresponding target nuclides are strongly activated by thermal and epithermal neutrons, and (3) the product radionuclides give rise to very complex spectra. Further, the sensitivity of instrumental NAA for Ta and W is such, that it is not only sufficient for the analysis of niobium samples of highest purity, containing still 0.1-6 ppm Ta and 2-100 ppb W [22] but, according to the limits of quantitative determination, it would be adequate to determine contents of both elements even slightly below 1 ppb, if niobium of this purity grade were available. This is, generally, one of the best examples of solving an extremely difficult analytical problem in a simple way by instrumental NAA.

The determination of other impurities in niobium is possible only by a radiochemical approach   involving separations of the radionuclides produced in an irradiation.

In our laboratory, we have found it meaningful to develop three different techniques based on the production and separation of indicator radionuclides (1) with long half-lives, (2) medium half-lives and (3) short half-lives. In all procedures of radiochemical NAA of niobium, it is a necessity to remove first the radionuclides of niobium, tantalum and tungsten representing normally the dominating radioactivity.

Table 4. Survey of applications of activation techniques to analysis of refractory metals

● technique very well suited,   ○ technique to a certain extent applicable,
— technique has little significance

Problem to be solved	Activation technique					
	INAA	RNAA	ICPAA	RCPAA	FNAA	PhAA
Niobium						
Determination of main metallic impurities (Ta, W)	●	●	○	○	−	−
Determination of light elements (B, C, N, O)	−	−	○	●	○	●
Determination of other relevant impurities	−	●	●	●	○	○
Tantalum						
Determination of main metallic impurities (Nb, W)	−	○	●	●	−	−
Determination of light elements (B, C, N, O)	−	−	○	●	○	●
Determination of other relevant impurities	−	●	○	●	−	○
Molybdenum and Tungsten						
Determination of main metallic impurities	−	●	−	●	−	−
Determination of light elements (B, C, N, O)	−	−	−	●	○	●
Determination of other relevant impurities	−	●	−	●	−	−

Several possibilities have been investigated, i.e., separation of Nb, Ta and W by ion exchange on a Dowex-1 column from a HF, a HF/HNO$_3$, and a HF/CH$_3$OH solution [23,24], and extraction of Nb and Ta from a HF solution with diantipyrylmethane [25]. They have then become the basic components of different separation schemes for radiochemical NAA.

A procedure [23] involving a long irradiation in a medium or high-flux reactor (in our case: a 42-days' irradiation with a thermal neutron flux of $8 \cdot 10^{13}$n cm^{-2}s^{-1}) and a separation shown in Figure 2 allows to achieve limits of detection as low as 10 ppt for Cr, 1.5 ppb for Fe and 4 ppt for Co if the specific separation in the second step is also applied. However, for the determination of contents of these elements which are present even in the highest purity niobium, it is sufficient to count the eluate after the first separation step by γ-ray spectrometry.

A number of elements yielding indicator radionuclides of medium half-lives, such as Na, K, Mn, Ni and Cu can be determined using a procedure [26] consisting of a 12-24 h irradiation and a two-step separation procedure for removal of the radionuclides of niobium, tantalum and tungsten, which does not require the transfer into the HCl medium and is therefore more rapid. Limits

of detection <1 ppb are achieved for Na, Mn and Cu, <0.1 ppm for K and Ni.

These two radiochemical activation methods, together with the instrumental NAA for the determination of Ta and W, have been used for checking the efficiency of a three-step purification technique for production of extremely pure niobium developed in recent years in Laboratorium für Reinststoffe, Max-Planck-Institut für Metallforschung, Stuttgart, F.R.G. [27], which includes the following steps:
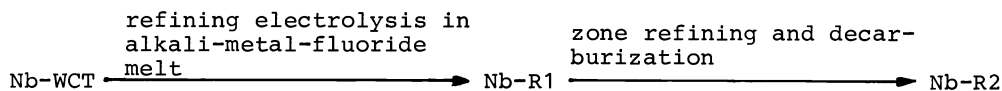
$$\text{Nb-WCT} \xrightarrow{\substack{\text{refining electrolysis in}\\ \text{alkali-metal-fluoride}\\ \text{melt}}} \text{Nb-R1} \xrightarrow{\substack{\text{zone refining and decar-}\\ \text{burization}}} \text{Nb-R2}$$

Table 5. Survey of (n,γ) reactions induced on refractory metals

Reaction	$\sigma_{th.}$ barns	RI, barns	Half-life	Major X- and γ-rays, MeV	Intensity %	Activity produced in 1-h irradiation dps/g a)
Niobium						
^{93}Nb$(n,\gamma)^{94m}$Nb	0.15	8.4	6.26m	0.0166 X 0.0187 X (o.l. 3)	33.0 6.0	2.1×10^9
^{93}Nb$(n,\gamma)^{94}$Nb	1.15	8.5	2×10^4a	0.7025 0.8711	100.0 100.0	4.0×10^2
Molybdenum						
^{92}Mo$(n,\gamma)^{93m}$Mo	$<$0.006	–	6.9h	0.2633 0.6846 1.4772 (o.l. 8)	61.2 91.9 99.4	$<5.4 \times 10^6$
^{98}Mo$(n,\gamma)^{99}$Mo	0.13	1.3	66.0h	0.0184 X 0.1811 0.7397 (o.l. 30)	6.5 6.0 13.0	2.4×10^7
$\downarrow \beta^-$						
^{99m}Tc			6.0h	0.1426 (o.l. 6)	85.0	
^{100}Mo$(n,\gamma)^{101}$Mo	0.2	4.2	14.6m	0.1920 0.5908 1.0124 (o.l. 42)	25.0 20.0 25.0	1.6×10^9
$\downarrow \beta^-$						
^{101}Tc			14.0m	0.3068 1.6170 2.2442 (o.l. 39)	91.0 10.0 12.0	
Tantalum						
^{181}Ta$(n,\gamma)^{182m}$Ta	0.01	0.28	16.0m	0.0575 X 0.1467 0.1717 (o.l. 6)	44.0 40.0 42.0	4.9×10^8
^{181}Ta$(n,\gamma)^{182g}$Ta	21.0	710	115.0d	0.0677 1.1212 1.2213 (o.l. 41)	43.0 37.0 28.9	2.9×10^8
Tungsten						
^{180}W$(n,\gamma)^{181}$W	3.5	200	121.2d	0.0563 X 0.0575 X 0.0652 X (o.l. 4)	22.0 40.0 13.0	7.6×10^4
^{184}W$(n,\gamma)^{185g}$W	1.8	22	75.1d	0.1254	0.02	8.7×10^6
^{186}W$(n,\gamma)^{187}$W	37.8	410	23.8h	0.0611 0.4795 0.6857 (o.l. 21)	12.8 26.6 32.0	1.2×10^{10}

a) At the end of the irradiation and assuming $\bar{\phi}_{th}= 10^{13}$n cm^{-2}s^{-1} and $\bar{\phi}_{epi}= 2 \times 10^{11}$n cm^{-2}s^{-1}

o.l. = other lines

```
                    ┌─────────────────────────┐
                    │ Nb-Sample (max. 600 mg) │
                    └─────────────────────────┘
                                │
                       Surface decontamination
                                │
                Addition of 0.5 mg of Cr, Fe and Co carriers
                                │
              Dissolution of the sample in 10 ml HF/HNO₃ 9:1
                                │
                Addition of 1.5 mg of Cr, Fe and Co carriers
                                │
                   Transfer into 10 ml 2N HF solution
                                │
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Pretreatment of the resin: Dowex 1 (X4, 50/100 mesh)
100 ml 8N HCl   Ø = 1 cm
100 ml H_2O filling height = 20 cm
150 ml 2N HF   in 2N HF

                       Elution with 2N HF

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        ┌──────────────────────────────┐
        │ 50 ml Eluate : Cr, Fe, Co, Ir │──────► γ-ray Spectrometry
        └──────────────────────────────┘
                                │
                   Transfer into 8 ml 8N HCl
                                │
```

Pretreatment of the resin: Dowex 1 (X4, 50/100 mesh)
100 ml 8N HCl   Ø = 1 cm
100 ml H_2O filling height = 20 cm
100 ml 8N HCl   in 8N HCl

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    1. Elution with        2. Elution with        3. Elution with
       8N HCl                  4N HCl              0.1N HCl/0.1% N₂H₂
          │                       │                      │
  ┌───────────────────┐  ┌─────────────────┐   ┌──────────────────┐
  │ 50 ml Eluate: Cr,Ir│ │ 40 ml Eluate: Co│   │ 50 ml Eluate: Fe │
  └───────────────────┘  └─────────────────┘   └──────────────────┘
          │
  Transfer into 5 ml
  1N HCl, Cl₂-saturated
          │
  Addition of 1 g Dowex 1
  Cl⁻-form, Cl₂-saturated
          │
       Filtration
      ┌───────┴────────┐
┌──────────────┐ ┌─────────────────────┐
│ Resin : Ir   │ │ 10 ml Filtrate : Cr │
└──────────────┘ └─────────────────────┘
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                       Evaporation to 5 ml

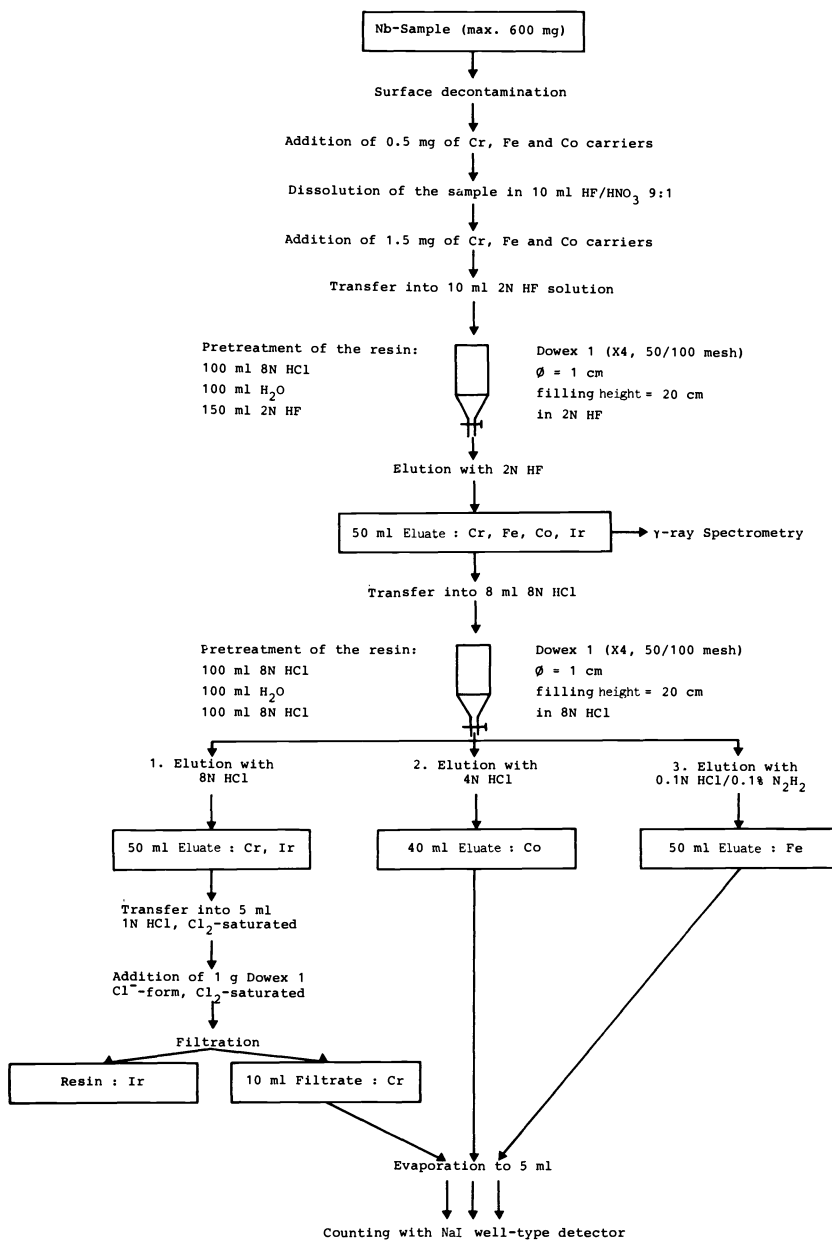   Counting with NaI well-type detector

Figure 2. Sample processing scheme for ion-exchange of Cr, Fe and Co
from a niobium matrix

The results are summarized in Table 6 and can be interpreted as follows. The initial material, Nb-WCT, was obtained by remelting under vacuum in an electron beam furnace, in which process metallic impurities having higher vapor pressure evaporate at the applied temperatures. This is the reason for their low contents. By the refining electrolysis, leading to Nb-R1, the main impurities, Ta and W are extensively removed but in the case of some elements, such as Fe, Co and Cr, contaminations are involved, which, however, are removed by following zone refining in ultra vacuum.

Table 6.   Analysis of niobium of different purity grades

Element	Nb-WCT	Nb-R-1	Nb-R-2
Na	10.5 ± 0.4 ppb	-	11.5 ± 4.9 ppb
Cr	1.7 ± 0.5 ppb	3.6 - 16.7 ppb	10 - 24.7 ppt
Mn	23 ± 10 ppb	-	80 - 90 ppt
Fe	15.5 ± 3.0 ppb	0.6 - 1.8 ppm	2 - 6.6 ppb
Co	53.9 ± 2.0 ppt	0.2 - 1.6 ppb	4 - 19.0 ppt
Cu	60.5 ± 6.6 ppb	20 - 50 ppb	3.5 - 4.5 ppb
Ta	163 ppm	5.5 - 6.0 ppm	0.9 - 5.8 ppm
W	7.5 ppm	60 - 70 ppb	10 ppb

Very recently, it was possible to develop a rapid radiochemical neutron activa-
tion technique for the determination of Mg, Al, Ti, V, Co, Cu, Se, Rb and Mo
in niobium [28], making use of short-lived indicator radionuclides
($T_{1/2}$= 2 - 20 min). The radionuclides ^{94m}Nb ($T_{1/2}$= 6.26 min) and ^{182m}Ta ($T_{1/2}$= 16min)
produced with high yields in the irradiations are separated on a Dowex-1 co-
lumn from a HF/HNO_3 mixture with decontamination factors better than 10^6. After
the separation, the eluate is counted first using a Ge(Li)-detector then with
an intrinsic Ge-detector. The limits of detection for the above elements lie
between 0.1 ppb (for V) and 60 ppb (for Mo). Also, this technique has been ap-
plied to analyse   niobium samples of different purity grades.

By etching or radiography studies on a neutron-irradiated sample, information
can be obtained about the distribution of the impurities in the matrix. For
instance, colored autoradiography has been used to investigate the distribu-
tion of tantalum and tungsten in niobium [29]. The continuous shades of gray in
the conventional autoradiograms are transformed into different color shades.
The quantitative evaluation is based on the dependence of the color on the
concentration of the investigated element. However, it should be mentioned
that this technique can be successfully used only in cases when an intense
beta emitter   is produced from the impurity in question.

For analysis of other refractory metals, NAA is not as useful   as for nio-
bium analysis. As can be seen from Table 5, the possibilities are limited
for instrumental NAA in the case of molybdenum. Two approaches can
be considered to avoid the problem of high matrix activity; either very
short irradiations (10s) or long cooling (50-100 days). Lenshkina et. al.
[30] determined Hf and W in molybdenum by instrumental NAA counting the short
lived radionuclides ^{179m}Hf ($T_{1/2}$=18.7 s) and ^{183m}W ($T_{1/2}$=5.3 s) after irradiation
for 5-10 sec. At a thermal neutron flux of $4 \cdot 10^{11} n cm^{-2} s^{-1}$, they reported
limits of detection of 0.1 ppm and 6 ppm, respectively, which are not low
enough for analysing high purity molybdenum. Though the second approach (long
cooling times), as the literature evaluation indicated, has not yet been app-
lied, it should enable the determination of some elements on the basis of long-
lived indicator radionuclides such as ^{59}Fe ($T_{1/2}$=44.4 d), ^{60}Co ($T_{1/2}$=5.27 Y), ^{181}Hf
($T_{1/2}$=42.2 d), ^{182}Ta ($T_{1/2}$=115.0 d) and some others.

Radiochemical NAA has been applied to the determination of Na (LD=5ppb) and K
(LD=50 ppb) in molybdenum [31]. Radiochemically pure ^{24}Na and ^{42}K are separa-
ted by combined anion- and cation exchange. By a method involving a 250-h irra-
diation of 0.2 g molybdenum with a neutron flux of $2 \cdot 10^{13}$ and a separation by
coprecipitation and ion exchange, P, Cr, Co, Fe, Zr, Hf, Ta and Th can be de-
termined; the limits of detection are between 0.5 and 0.01 ppm [32]. Another
interesting technique, based on a successive displacement chromatography and

substoichiometric separation, can detect Mn, Zn, Cd, Ag, Hg and Co in molybde-
num [33]. Fedoroff [34] described a technique for the determination of Na, Mn,
Ni, Cu and W in molybdenum based on the specific separation of the appropriate
indicator radionuclides by precipitation and ion exchange, and counting the
fractions with NaI(Tl) detector; for the detection of ^{65}Ni, a β-counter was
used. Samadi et.al. [35] developed a radiochemical NAA technique for the deter-
mination of Re in molybdenum, based on a two-step separation, in which Re and
Tc are first extracted by acetone from a solution of the irradiated molybdenum
containing NaOH, and then Re and Tc are separated by ion exchange from 0.1 M-
HCl containing 5% NH_4SCN. Contents of Re below 1 ppb can be determined.

Instrumental NAA has little chance to be used for analysis of tantalum and
tungsten. Even the radiochemical approach is not without problems. Because
of extremely high matrix activities, in the separation, special measures must
be taken for protection (using manipulators, shielding, hot cells) and, for
the same reason, extraordinarily high decontamination factors are required in
the separations. The high thermal cross-sections and resonance integrals cause
a strong attenuation of the neutron flux within the sample, even when it is in
small amounts: an error of -5% is caused by as little as 8 mg tantalum and 10 mg
tungsten; an error of -10% by 70 mg tantalum and 80 mg tungsten. This means
that corrections for the selfshielding effect must be carried out. This ex-
plains why relatively little use has been made of NAA for analysis of these
two matrices. For the analysis of tungsten, the most efficient technique has
been developed by Cosgrove and Morrison [38] enabling the determination of Fe,
Zn, As and Mo by using precipitation with α-benzoinoxime and extractions, and
by Döge and Große-Ruyken [32] for the determination of P, Cr, Fe, Co, Zr, Hf,
Ta and Th, at levels between 1 ppm and 0.01 ppm. The above discussed and some
other applications of radiochemical NAA to analysis of refractory metals are
surveyed in Table 7.

14-MeV neutron activation

This technique is suitable for the instrumental determination of oxygen con-
tents down to ppm level in all four considered refractory metals, via the reac-
tion $^{16}O(n,p)^{16}N$, in spite of relatively strong activation of the matrices.
It is made possible by 2 favorable circumstances: (1) The short half-life of
the indicator radionuclide ^{16}N (T=7.2 s) enables to achieve a rapid saturation,
whereas the saturation factors of the matrix radionuclides, due to their sig-
nificantly longer half-lives, are much   lower, and, consequently also the
induced matrix activity. (2) In the decay of ^{16}N, high energy γ-rays, mainly
6.1 and 7.1 MeV, are emitted, which are essentially higher than those emitted
by the matrix nuclides, so that the low energy region can be discriminated and
the determination made free from instrumental interferences. An additional ad-
vantage of the high γ-energies is the possibility to use large samples with-
out significant corrections for γ-ray attenuation. Sample amounts up to 120 g
of niobium [44], 60 g of molybdenum [45], 88g of tantalum [46], and 8 g of tung-
sten [47] have been used for analysis. Assuming a 14-MeV neutron flux of
$10^9 n cm^{-2}s^{-1}$, an activity of 1.1 dps per μg oxygen is produced in a   15 sec ir-
radiation. Taking into account the activity losses during the transport and the
surface etching, the minimum total amount of oxygen necessary for detection is
10-50 μg. Using sample amounts usually available for analysis, oxygen contents
down to a few ppm, under optimum conditions to ~0.5 ppm, can be detected. The
14-MeV NAA has been developed into a very reliable routine method as shown by
a round-robin test for the determination of oxygen in molybdenum (14 ppm) by
five different techniques [48].

Activation with charged particles and photons

The most significant application of CPAA is, without doubt, in   the deter-
mination of light elements ($3 \leq Z \leq 9$), of which B, C, O and N are of current
interest. For the determination of each of these elements, several extremely
sensitive reactions are available. Table 8 summarizes the most important reac-
tions for Li, B, C, N and O and some examples of their applications to the
analysis of refractory metals.

A controlled and reliable post-irradiation removal of the surface contamina-
tion and the recoil atoms is of primary importance. Experiences of the re-
cent years show that this problem can be considered as satisfactorily solved.
The most difficult task to be solved in many practical cases is the elimina-
tion of, or at least reliable correction for, nuclear interferences.

Table 7.   Survey of application of radiochemical NAA to analysis of refractory metals

Matrix	Elements determined and separations involved a)	Contents	Detection limits	Ref.
Nb	Mg, Al, Ti, V, Co, Cu, Se, Rb, Mo (I)	0.4 ppb (Co) – 1.2 ppm (Mo)	0.1 ppb (V) – 60 ppb (Mo)	[28]
	Na, K, Mn, Ni, Cu, (I, E)	85 ppt (Mn) – 0.56 ppm (Cu)	30 ppt (Mn) – 0.1 ppm (Ni)	[26]
	Cr, Fe, Co (I)	4 ppt (Co) – 1.8 ppm (Fe)	4 ppt (Co) – 1.5 ppb (Fe)	[23]
	Fe, Co, Cu, Ta, W (I)	1 ppm (Cu) – 10^4 ppm (Ta)	---	[39]
Mo	Na, Mn, Ni, Cu, W (I, P)	30 ppb (Mn) – 220 ppm (W)	0.1 ng (Mn) – 7 ng (Ni)	[34]
	P, Cr, Fe, Co, Zr, Hf, Ta, Th (P, I)	70 ppb (Ta) – 260 ppm (Fe)	10 ppb (Ta) – 0.5 ppm (Zr)	[32]
	Mn, Cu, Zn, Ag, Cd, Hg (E)	---	10 ppb or higher	[33]
	Na, K (I)	9 ppm (K) – 13 ppm (Na)	5 ppb (Na), 50 ppb (K)	[31]
	Al (I)	0.6 – 40 ppm	0.1 ppm	[40]
	Pd (I, P)	1 ppm	0.6 ng	[41]
	S (I, P)	80 – 100 ppb	---	[37]
	W (E)	12 – 1500 ppm	---	[36]
	Re (E, I)	2 – 930 ppb	1.5 ppb	[35]
Ta	Na, Mn, Nb, W (E)	0.4 ppm (Mn) – 87 ppm (Nb)	---	[42]
	Na, Cr, Mn, Cu, W (I)	20 ppb (Mn) – 60 ppm (W)	---	[39]
W	P, Cr, Fe, Co, Zr, Hf, Ta, Th (P, I)	20 ppm (Ta) – 9 ppm (Fe)	10 ppb (Ta) – 0.5 ppm (Zr)	[32]
	Fe, Zn, As, Mo (P, E)	3 ppm (As) – 2000 ppm (Fe)	---	[38]
	Na, K (I)	1.8 ppm (Na) – 2.5 ppm (K)	5 ppb (Na), 50 ppb (K)	[31]
	Ga (E)	2 ppb – 18 ppm	---	[43]
	Mo (E, I)	1.4 – 87 ppm	0.1 ppm (10 ng)	[44]
	Re (E)	0.2 ppb – 2×10^5 ppm	0.2 ppb	[35]

a)   I = ion exchange,   E = extraction,   P = precipitation

In many instances, interfering reactions can be avoided or at least reduced to a negligible degree, by the choice of projectile   and its energy. The op-timum reaction is normally that which allows to meet the best compromise bet-ween sensitivity and selectivity.

Table 8. Survey of important charged-particle and photon induced reactions for the determination of light elements and their application to analysis of refractory metals

Element	Principal reactions	Projectile energy, MeV	Detection limit, ppb	Interfering elements	Refractory metal analyzed (a selection)
Li	^{7}Li(p,n)^{7}Be	14	0.8	B,N	Nb [49]
	^{6}Li(d,n) / ^{7}Li(d,2n) }^{7}Be a)	15	6	B	Nb [49]
B	^{11}B(p,n)^{11}C	10-15	0.1-0.5	N	
	^{10}B(d,n) / ^{11}B(d,2n) }^{11}C a)	10-20	0.1-1	N,C	Ta [50]
	^{10}B(p,α) / ^{11}B(p,αn) }^{7}Be	14	8	Li,N	Nb [49]
	^{10}B(d,αn) / ^{11}B(d,α2n) }^{7}Be	15	15	Li	Nb [49]
C	^{12}C(d,n)^{13}N a)	5-20	0.2-0.5	N,O	Nb,Ta, W [51],Mo, W [52]
	^{12}C(^{3}He,α)^{11}C	10-20	0.5-2	Be,B,N,O	
	^{12}C(α,αn)^{11}C	34-42	1-10	Be,B,N,O	
	^{12}C(γ,n)^{11}C	18.7	1-5	N,O	Nb,Mo,Ta,W [53], Nb,Mo[54] W [13]
N	^{14}N(p,n)^{14}O	12	400	None at E<20MeV	Nb, Mo, T, W [55]
	^{14}N(p,α)^{11}C	10-15	0.1-0.5	B	Ta [50]
	^{14}N(d,n)^{15}O	10-20	0.05-0.5	B,C	
	^{14}N(γ,n)^{13}N	10.6	10-50	O,F	Nb, Mo, Ta, W [53]
O	^{18}O(p,n)^{18}F	10-15	10-100	F	
	^{16}O(p,α)^{13}N	10-15	0.5-2	C,N	
	^{16}O(d,n)^{17}F	10-20	0.1-1	F	
	^{16}O(t,n)^{18}F	3-3.5	0.5-25	None at E<4MeV	Mo [56]
	^{16}O(^{3}He,p)^{18}F a)	10-20	0.5-2	F,Na,Mg,Al	Nb[57],Mo[58],W[52]
	^{16}O(α,d)^{18}F	34-45	0.5-1	N,F,Na,Mg,Al,Si	Mo [59]
	^{16}O(γ,n)^{15}O	15.7	10-50	Ne,F	Nb,Mo,Ra,W [53],Nb,Mo [54], Ta,W [13], W [52]

a) optimum charged-particle-induced reaction for the determination of the given element

Photon activation analysis is the only alternative technique to CPAA for the
determination of light elements (C, N, O, F) at extremely low concentration.
In the analysis of refractory metals, so far, PAA has almost exclusively been
used for this purpose. The basic data on this technique are also included in
Table 8. An advantage of the PAA in comparison with CPAA is to be seen in the
possibility to irradiate large volume samples and their "quasi-uniform" acti-
vation which may be an important factor in the improvement of accuracy.
The ultimate contribution of CPAA and PAA to the progress made in the determi-
nation of light elements in refractory metals (and in solids generally) has
become definitely clear after results were obtained by various techniques from
interlaboratory collaborative investigations - so called round-robins carried
out in recent years. They lead to the conclusion that, at the very low content
level (<1 ppm), even   with highest care   , it is not possible to
obtain acceptably accurate results by chemical techniques, obviously because
of the inability to solve the problem of blank and perfect surface decontami-
nation. In general, the lower the content to be determined, the larger the
deviation between the results obtained by activation and chemical techniques.

Table 9. Results obtained in the determination of
C in molybdenum and tungsten by photon
activation analysis and fusion extraction

Matrix	Method	Content determined, ppm
Mo	Activation: $^{12}C(\gamma,n)^{11}C$	0.2 - 0.4
	Fusion extraction	5 - 18
W	Activation: $^{12}C(\gamma,n)^{11}C$	0.01 - 0.06
	Fusion extraction	3.4 - 10

Table 10. Comparison of results obtained in the determi-
nation of C and O in molybdenum and tungsten
by CPAA and PAA

Matrix	Element determined	Method	Content determined, ppb	Reference
Mo	C	CPAA	72 ± 32	[52]
		PAA	130 ± 60	
W	C	CPAA	$<$ 15	[52]
		PAA	30 ± 30	
	O	CPAA	66 ± 11	
		PAA	74 ± 7	
W	O	CPAA	470 ± 260 410 ± 210	[13]
		PAA	480 ± 250 700 ± 150	

In Table 9, results for the determination of C in molybdenum and tungsten obtained by PAA and by the conventional combustion technique are given as examples. On the other hand, good agreement of results obtained by activation techniques and fusion extraction was achieved in the determination of 14 ppm of oxygen in molybdenum [49]. In recent years, CPAA and PAA have been developed as very reliable techniques for the determination of light elements. For example, results obtained for the determination of contents < 1 ppm by CPAA and PAA agree well with each other, as can be seen from Table 10.

In recent years, CPAA has increasingly been used also for the determination of medium and heavy elements in refractory metals. The application to analysis of tantalum is,without doubt,of greatest practical significance,as the analysis of this matrix by thermal NAA is very inconvenient. We applied instrumental proton activation analysis for trace characterization of high purity tantalum [60]. It is based on the analysis of the γ-ray spectra of the radionuclides by bombarding thick samples with 15 MeV protons. The technique provides analysis with high sensitivity and selectivity for most trace elements of major interest, as can be seen from Table 11.

Table 11. Instrumental proton activation analysis of tantalum

Element determined	Activation reaction	$T_{1/2}$	Major γ-rays, MeV	Content determined, [a] ppm	Experimental LD [b], ppm
Ti	$^{48}Ti(p,n)^{48}V$	16.0 d	0.983 1.312	0.09 ± 0.02	0.02
Fe	$^{56}Fe(p,n)^{56}Co$	78.5 d	0.847 1.238 2.598	0.8 ± 0.15	0.1
Zr	$^{90}Zr(p,n)^{90}Nb$	14.6 h	1.129 2.319	0.12 ± 0.02	0.005
Nb	$^{93}Nb(p,n)^{93m}Mo$	6.9 h	0.263 0.685 1.477	33 ± 3	0.3
Mo	$^{96}Mo(p,n)^{96}Tc$	4.3 d	0.778 0.850 0.812	0.7 ± 0.1	0.2
W	$^{182}W(p,n)^{182}Re$	13.0 h	1.122 1.222	due to strong interference not meaningful	
	$^{182}W(p,2n)^{181}Re$	19.0 h	0.366	6.6 ± 1.4	0.5

a) VP grade tantalum, MPC

b) Irradiation condition assumed: Proton energy = 15 MeV
    beam current   ~ 2 μA
    irradiation time ~2.5 h

In the determination of Mo, in addition to ^{96}Tc, ^{92}Tc ($T_{1/2}$= 4.4 m), ^{94m}Tc ($T_{1/2}$=53 m), ^{94}Tc ($T_{1/2}$=4.9 h), ^{95}Tc ($T_{1/2}$=20 h), and ^{99m}Tc ($T_{1/2}$=6 h) can also be used as indicator radionuclides [61]. One of the important features of this multireaction activation technique is the possibility of checking the accuracy with regard to nuclear and instrumental interferences and also with regard to the depth distribution. Distribution studies are possible by the fact that the dependence of the production of the indicator radionuclide on the projectile penetration depth,differs for the individual principal reactions. Thus, by

comparison of the results obtained via different reactions, conclusions can be made on the depth distribution of molybdenum in tantalum.

Another meaningful application of instrumental proton activation analysis is that to analytical characterization of niobium [62]. However, niobium itself can also be activated by proton irradiation. The reaction ^{93}Nb(p,n)^{93m}Mo cannot practically be avoided but, in this instance, counting of indicator radionuclides having half-lives longer than 14 h is possible after a cooling time of 50-70 h. For the instrumental performance, it is necessary to minimize the production of the long lived ^{92m}Nb (T=10.2 d) produced via the ^{93}Nb(p,pn) reaction. It occurs only to an insignificant extent up to a proton energy of 12 MeV. By making use of both the γ-ray and X-ray spectrometry, 12 elements were analysed in niobium of very high purity   (Table 12).

Table 12. Instrumental proton activation analysis of niobium using both γ-ray and
           X-ray spectrometry

Element determined	Indicator radionuclide	Rays counted, keV	Detector used	Content determined,[a] ppm	Experimental LD[b], ppm
Ti	^{48}V	983 1312	Ge(Li)	0.32 ± 0.14	0.04
V	^{51}Cr	320	Ge(Li)	0.55 ± 0.23	0.13
Cr	^{52}Mn	1434	Ge(Li)	0.7 ± 0.2	0.05
Fe	^{56}Co	1238 1771 2598	Ge(Li)	1.4 ± 0.2	0.1
Zr	^{90}Nb	141 2319	LED Ge(Li)	1.6 ± 0.2 1.5 ± 0.3	0.5 0.4
Mo	^{96}Tc	778 812	Ge(Li)	5.2 ± 0.8	0.2
Pd	^{106m}Ag	21.2 X 23.9 X	LED	N.D.	0.2
Sn	^{120m}Sb	25.2 X 89.8	LED	N.D.	0.2
Sb	^{121m,g}Te, ^{123m}Te	26.3 X 27.4 X 159	LED	N.D.	0.03
Hf	^{177}Ta	54.6 X	LED	N.D.	0.13
Ta	^{181}W	56.3 X 65.2 X	LED	321	4.5
W	^{182m,g}Re	59.3 69.1 100.1	LED	80.8 ± 7	0.3
		1122 1222	Ge(Li)	88.2 ± 19	38

a) good purity niobium, Teledyne Wah Chang Albany, Ore.
b) Irradiation conditions assumed: proton energy   = 12 MeV
                                   beam current   = 4 μA
                                   irradiation time = 1.5 h

In the radiochemical approach, the limits of detection can be improved and a number of additional elements determined. For instance, by radiochemical proton activation analysis with 13 MeV protons, involving a two-step separation by ionexchange from HF and HCl medium, as little as 0.2 ppb of Cr, 5 ppb of Fe and 15 ppb of Cu can be detected [63].

Table 13 summarizes the application of CPAA to analysis of refractory metals excluding the determination of light elements.

Table 13.   Survey of applications of CPAA to analysis of refractory metals for medium and heavy elements

Matrix	Type and energy of particles	Analytical approach	Elements determined	Range of contents determined (a) and of LD (b), ppm				Reference
Nb	p, 12 MeV	I	Ti,V,Cr,Fe,Zr, Mo,Ta,W,Hf	(a) 0.3 (b) 0.04	(Ti)- 321 (Ti)- 4.5	(Ta) (Ta)		[62]
	p, 10 MeV	I	Mo,W	(a) 71 (b) 0.2	(Mo), 72 (Mo), 1.7	(W) (W)		[64]
	p, 13 MeV	R	Cr,Fe,Cu	(a) 0.03 (b) 0.0002	(Cr)- 4.4 (Cr)- 0.015	(Fe) (Cu)		[63]
Ta	p, 15 MeV	I	Ti,Fe,Zr,Nb, Mo,W	(a) 0.09 (b) 0.005	(Ti)- 32 (Zr)- 0.5	(Nb) (W)		[60]
	p, 11 MeV	I	Ti,Cr,Fe,Nb, Mo,W	(a) 20 (b) 0.2	(Ti)-2000 (Ti)- 15	(Nb) (W)		[65]
	p, 10 MeV	I	Nb,Mo	(a) 2 (b) 0.07	(Mo), 39 (Mo), 0.4	(Nb) (Nb)		[64]
	^{3}He, 14 MeV	I	Fe,Nb	(a) 6 (b) not given	(Fe), 16	(Nb)		[66]
	p, 11 MeV	R	Ca,Ti,V,Cr,Fe, Cu,Nb,W	(a) 20 (b) 0.003	(Ti)-2000 (Ca)- 0.6	(Nb) (Cu)		[65]
W	^{3}He, 14 MeV	I	Fe,Ni,Zn,Mo	(a) 0.9 (b) not given	(Zn)- 4	(Mo)		[66]

I = Instrumental; R = Radiochemical

CONCLUSIONS

Activation analysis techniques have made ultimate contribution to the progress achieved in trace analysis of refractory metals. The reasons for this are some unique features of activation techniques including high detection sensitivity, freedom from blank and the ability to remove surface contamination. Because of these factors, activation analysis offers the best choice of all trace analytical techniques for obtaining accurate results, even at extremely low concentrations. At present, most of the trace impurities in refractory

metals of high purity can be determined exclusively with activation techniques, as is evident from examples given in Table 14 for niobium. Another principal contribution of the activation techniques is to be seen in their use for assessing the reliability and accuracy of other techniques.

Table 14. Comparison of the best detection limits of activation and non-activation techniques for the determination of selected elements in niobium

Element	Detection limit, ppb	
	Best activation technique	Best non-activation technique
Li	1	-
B	8	20
O	1	10^3
Na	0.08	-
Al	5	-
V	0.1	-
Cr	0.01	4000
Fe	1.5	300
Co	0.004	100
Cu	0.2	10
Mo	60	0.5
Hf	0.01	2×10^4
Ta	0.1	400
W	0.5	500

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