

# Chemical Effects on K /K X-Ray Intensity Ratio for $^{97m}\text{Tc}$ and $^{95m}\text{Tc}$

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II. 10 Chemical Effects on  $K_{\beta}/K_{\alpha}$  X-Ray Intensity Ratio For  $^{97m}\text{Tc}$  and  $^{95m}\text{Tc}$

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1. Introduction

Chemical effects on X-ray intensity ratio for the first transition elements have been studied in our laboratory in case of electron capture nuclides.<sup>1-3)</sup> Dependence of the  $K_{\beta}/K_{\alpha}$  ratios on valence states of chromium was found for the electron capture process of  $^{51}\text{Cr}$ . This phenomenon was utilized in chemical state analysis of recoil chromium by Collins et al.<sup>4)</sup>

In the previous study we have found chemical effect of  $K_{\beta}/\gamma_{140}$  for isomeric transition of  $^{99m}\text{Tc}$ .<sup>5)</sup> Slight variation of the ratio was observed from metallic molybdenum to molybdenum oxide. The phenomenon was the first case for the nuclides in the second transition elements.

This study aimed at finding the chemical effects on X-ray intensity ratios of cyclotron produced nuclides of technetium such as  $^{97m}\text{Tc}$  and  $^{95m}\text{Tc}$ .

2. Experimental

$^{97m}\text{Tc}$  and  $^{95m}\text{Tc}$  were produced by (d,xn) reactions in a molybdenum foil.  $^{95m}\text{Tc}$  was also produced by the  $^{93}\text{Nb}(\alpha,2n)^{95m}\text{Tc}$  reaction.  $^{97m}\text{Tc}$  decays to  $^{97}\text{Tc}$  (isomeric transition) with half-life of 90 days. 96 % of  $^{95m}\text{Tc}$  decays to  $^{95}\text{Mo}$  (electron capture) and 4 % to  $^{95}\text{Tc}$  (isomeric transition). Half-life of  $^{95m}\text{Tc}$  is 61d. Sufficient cooling time before measurement was necessary for decaying out of other technetium nuclides. X-ray measurement of deuteron-reaction-produced  $^{97m}\text{Tc}$  always involves slight contribution from the presence of  $^{95m}\text{Tc}$ , and it can be corrected by the measurement of  $^{95m}\text{Tc}$  produced by the ( $\alpha,2n$ ) reaction.

Si(Li) detectors (connected with 4k pulse-height analysers) were used for the measurement of K X-rays. Energies of characteristic X-rays of technetium are as follows:

$K_{\alpha 1}$	18.367 keV	$K_{\alpha 2}$	18.251 keV
$K_{\beta 1}'$	20.61 keV	$K_{\beta 2}'$	20.01 keV

Measurement was done so that counting statistical errors may be less than 1 %. The measured data were analysed by a computer program.

Irradiated molybdenum foils were submitted to chemical procedures involving sublimation in order to separate technetium in the sublimate.

3. Results and Discussion

The results of  $K_{\beta}/K_{\alpha}$  X-ray intensity ratio for  $^{97m}\text{Tc}$  (isomeric transition) are shown in Table 1. The data are corrected by subtracting the contribution from  $^{95m}\text{Tc}$ .

Variation of the ratio due to the chemical state is larger in  $K_{\beta 2}'/K_{\alpha}$  than in  $K_{\beta 1}'/K_{\alpha}$ . This is understandable because  $K_{\beta 2}'$  X-rays are emitted from the transition of outer electrons whereas  $K_{\beta 1}'$  X-rays are emitted from that of inner electrons. The former will be influenced more strongly by the chemical environment than the latter. It is interesting to see that the compounds of the same valence, i.e.  $K\text{TcO}_4$  and  $\text{Tc}_2\text{S}_7$  show different values of the ratio.

The  $K_{\beta}/K_{\alpha}$  intensity ratios for  $^{95\text{m}}\text{Tc}$  (electron capture) are shown in Table 2. The same inclination as  $^{97\text{m}}\text{Tc}$  is seen in the table.

The results obtained above can be interpreted by the Pauling's concept of ionicity which is available for the first transition elements.<sup>6)</sup> Calculated ratios for various Tc compounds to pertechnetate are compared with those experimentally obtained. Fairly good agreement between them shows that the chemical effects observed depend mainly on the difference of electronegativity between the technetium and counter atoms.

#### References

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Table 1.  $K_{\beta}/K_{\alpha}$  ratios for  $^{97m}\text{Tc}$

Compounds Valence	$K_{\beta_1}'/K_{\alpha}$	$K_{\beta_2}'/K_{\alpha}$
Tc metal (0)	$0.1695 \pm 0.0007$	$0.02894 \pm 0.00011$
$\text{K}_2\text{TcCl}_6$ (IV)	$0.1695 \pm 0.0007$	$0.02893 \pm 0.00017$
$\text{KTcO}_4$ (VII)	$0.1705 \pm 0.0004$	$0.02962 \pm 0.00017$
$\text{Tc}_2\text{S}_7$ (VII)	$0.1688 \pm 0.0003$	$0.02842 \pm 0.00024$

Table 2.  $K_{\beta}/K_{\alpha}$  intensity ratio for  $^{95m}\text{Tc}$

Compounds Valence	$K_{\beta_1}'/K_{\alpha}$	$K_{\beta_2}'/K_{\alpha}$
Tc metal 0	$0.1668 \pm 0.0005$	$0.02755 \pm 0.00004$
$\text{K}_2\text{TcCl}_6$ IV	$0.1678 \pm 0.0006$	$0.02702 \pm 0.00004$
$\text{KTcO}_4$ VII	$0.1685 \pm 0.0006$	$0.02815 \pm 0.00002$
$\text{Tc}_2\text{S}_7$ VII	$0.1668 \pm 0.0005$	$0.02686 \pm 0.00023$

Table 3. Relative value of  $K_{\beta_2}'/K_{\alpha}$  referred to that of pertechnetate

Compound	$K_{\beta_2}'/K_{\alpha}$ (calcd.)	$K_{\beta_2}'/K_{\alpha}$ (obtained)		
		$^{99m}\text{Tc}^*$	$^{97m}\text{Tc}$	$^{95m}\text{Tc}$
Tc metal/ $\text{KTcO}_4$	0.9432	0.9447	0.9770	0.9665
$\text{K}_2\text{TcCl}_6/\text{KTcO}_4$	0.9611	0.9428	0.9767	0.9706
$\text{Tc}_2\text{S}_7/\text{KTcO}_4$	0.9535	0.9396	0.9595	0.9326

\* Results obtained for the nuclide separated from neutron irradiated molybdenum.