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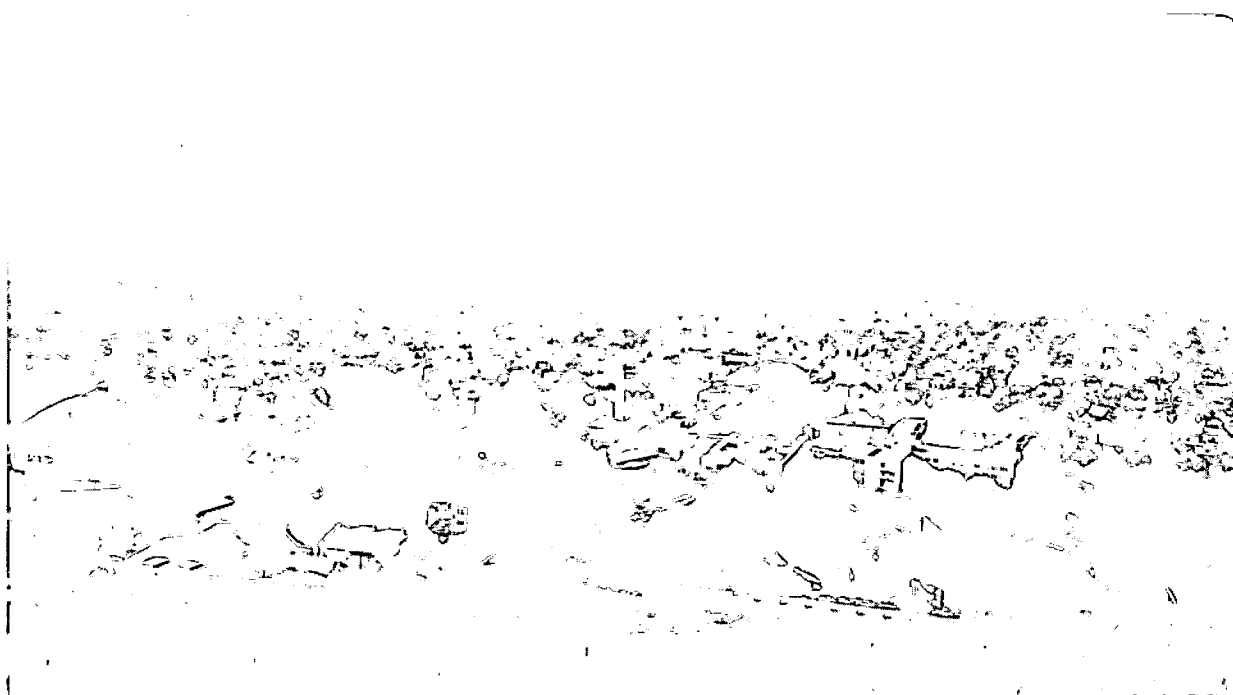
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### **Environmental Applications of XANES: Speciation of Tc in Cement After Chemical Treatment and Se After Bacterial Uptake**

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## Environmental Applications of XANES: Speciation of Tc in Cement After Chemical Treatment and Se After Bacterial Uptake

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# ENVIRONMENTAL APPLICATIONS OF XANES: SPECIATION OF Tc IN CEMENT AFTER CHEMICAL TREATMENT AND Se AFTER BACTERIAL UPTAKE

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## ABSTRACT

XANES (X-ray Absorption Near Edge Spectroscopy) has been employed to evaluate the efficacy of a process designed to encapsulate and reduce  $\text{TcO}_4^-$  in cement matrices, thereby immobilizing Tc. The oxidation state of Se following bioremediation of Se by bacteria has also been determined by XANES. The XANES measurements were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) and the National Synchrotron Light Source (NSLS) at the respective K edges of Tc (21.0 keV) and Se (12.7 keV). Comparison of the XANES spectra of Tc in untreated cement to Tc in slag treated cement and to the chemical shifts of reference materials, shows that the oxidation state of Tc is the same in both cements. Thus, the addition of a reducing agent to the cement formulation does not significantly reduce the  $\text{TcO}_4^-$ . The common soil bacterium, *Bacillus subtilis*, is known to incorporate Se on or within the cell wall when exposed to a Se(IV) solution. The Se XANES spectra of *B. subtilis*, as well as bacillus isolated from selenium rich soil, show that the organisms reduce selenite to the red allotrope of elemental Se.

## INTRODUCTION

X-ray Absorption Spectroscopy (XAS) techniques are useful, non-destructive probes employed to determine the oxidation states of materials from X-ray Absorption Near Edge Structure (XANES), and local structural information can be extracted from Extended X-ray Absorption Fine Structure (EXAFS) measurements.<sup>1</sup> XAS investigations are well-suited for the study of radioactive and hazardous materials systems in the hard X-ray regime since samples may be safely contained for *in-situ* measurements at storage ring facilities. XAS methodologies are compatible with low concentration samples and are also highly amenable for studies of solutions and amorphous materials, both of which are of importance for environmental purposes. Thus, these techniques provide an ideal means for detailed electronic and structural investigations of fission product materials and other environmentally-relevant materials systems.

In XANES, the energy of the absorption edge is directly related to the oxidation state of the atom of interest.<sup>1</sup> Two studies of environmental contaminant speciation utilizing XANES to determine oxidation states have been performed. The first investigation was to evaluate the effectiveness of a chemical reaction designed to slow the release of  $^{99}\text{TcO}_4^-$  in nuclear wastefrom cements. The liquid waste is encapsulated in the cement with a reducing agent intended to reduce the Tc(VII) to less soluble Tc(IV). Previous XANES measurements have

demonstrated that  $\text{CrO}_4^{2-}$  is quantitatively reduced to less soluble Cr(III) under these conditions.<sup>2</sup> The efficacy of the process was determined by measurements of wasteform cements with and without the reducing agent. The second investigation was to characterize the oxidation state of Se after microbial uptake from an aqueous solution by common soil bacteria, in order to provide information about the possible mechanisms of bioremediation.

## EXPERIMENTAL

The XANES measurements were performed at the storage rings of the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline 4-1 and the National Synchrotron Light Source on beamline X23A2. The Tc K edge (~21.0 keV) measurements were made exclusively on the wiggler branch beamline 4-1, utilizing Si(220) monochromator crystals detuned ~50% to reduce contributions from higher order harmonics. The Se K edge (~12.7 keV) spectra were recorded at the bend magnet beamline X23A2 at the NSLS with Si(311) monochromator crystals and at beamline 4-1 in an identical manner as for the Tc studies. The convoluted experimental resolution is ~3 eV for Tc, ~1 eV for Se at 4-1, and ~1 eV for Se at X23A2. The detection techniques employed ionization chambers for transmission measurements at both facilities. A single element Si detector and Stern Heald detector were employed for fluorescence measurements at SSRL only. All spectra were collected simultaneously with Se or Tc reference materials to establish the respective chemical shifts and to ensure photon energy calibrations. The edge positions were determined using the first derivative method. Data reduction was accomplished with the SSRL EXAFSPAK program suite.

The Tc cements were prepared and packaged at SREL, whereas the Tc reference materials were prepared at LBL and LANL. The untreated cement was prepared by combining 25 wt. % Portland cement, 25 wt. % fly ash, 50 wt. % of a simulated aqueous waste solution containing 1000 ppm  $^{99}\text{TcO}_4^-$ . The composition of the simulated wastestream has been reported elsewhere.<sup>2</sup> The cement containing the reducing agent was composed of 50 wt. % simulated waste solution, 20 wt. % fly ash, 10 wt. %  $\text{Ca}(\text{OH})_2$ , 10 wt. % Portland cement, and 10 wt. % blast furnace slag. Slag is a source of ferrous iron and sulfide, which is believed to reduce  $\text{TcO}_4^-$  to  $\text{TcO}_2$ . The  $\text{TcO}_2$  was prepared by the thermal decomposition of ammonium pertechnetate and the  $\text{TcO}_2$  sub-oxide by controlled electrodeposition. The samples were contained in thin-wall silica or polyethylene tubes, followed by the application of a heat shrink polyethylene tube. Vegetative cells of *B. subtilis* and of an unidentified bacillus isolated from Kesterson soil were exposed to aqueous Se solutions of different oxidation states, either selenite (IV) or selenate (VI). The bacteria did incorporate Se from the selenite growth solution, however, there was no uptake from the selenate solution. The bacteria were purified by repeated steps of centrifugation and washing. The centrifugal pellets were prepared for XANES by lyophilization and subsequent double encapsulation in polyethylene.

## RESULTS AND DISCUSSION

### Speciation of Tc in Wasteform Cement

The nuclide  $^{99}\text{Tc}$  is a by-product of nuclear fission, with large quantities of  $\text{TcO}_4^-$  stored for disposal as solid, low-level radioactive waste. Immobilization of  $^{99}\text{Tc}$  is essential for adequate disposal due to its long half-life ( $t_{1/2}=2 \times 10^5$  years) and the propensity for  $\text{TcO}_4^-$  to migrate in the geosphere.<sup>3</sup> One method for disposal involves microencapsulation of the liquid waste in a cement matrix.<sup>4</sup> In addition, chemical reduction of the mobile  $\text{TcO}_4^-$  to a less soluble  $\text{Tc}^{4+}$  species is desirable. However, reduction to a lower oxidation state requires chemical additives in the form of a reducing agent such as slag.

XANES spectra were collected from wasteform cements prepared at the SREL with and without slag from a simulated nuclear waste stream spiked with pertechnetate. The XANES

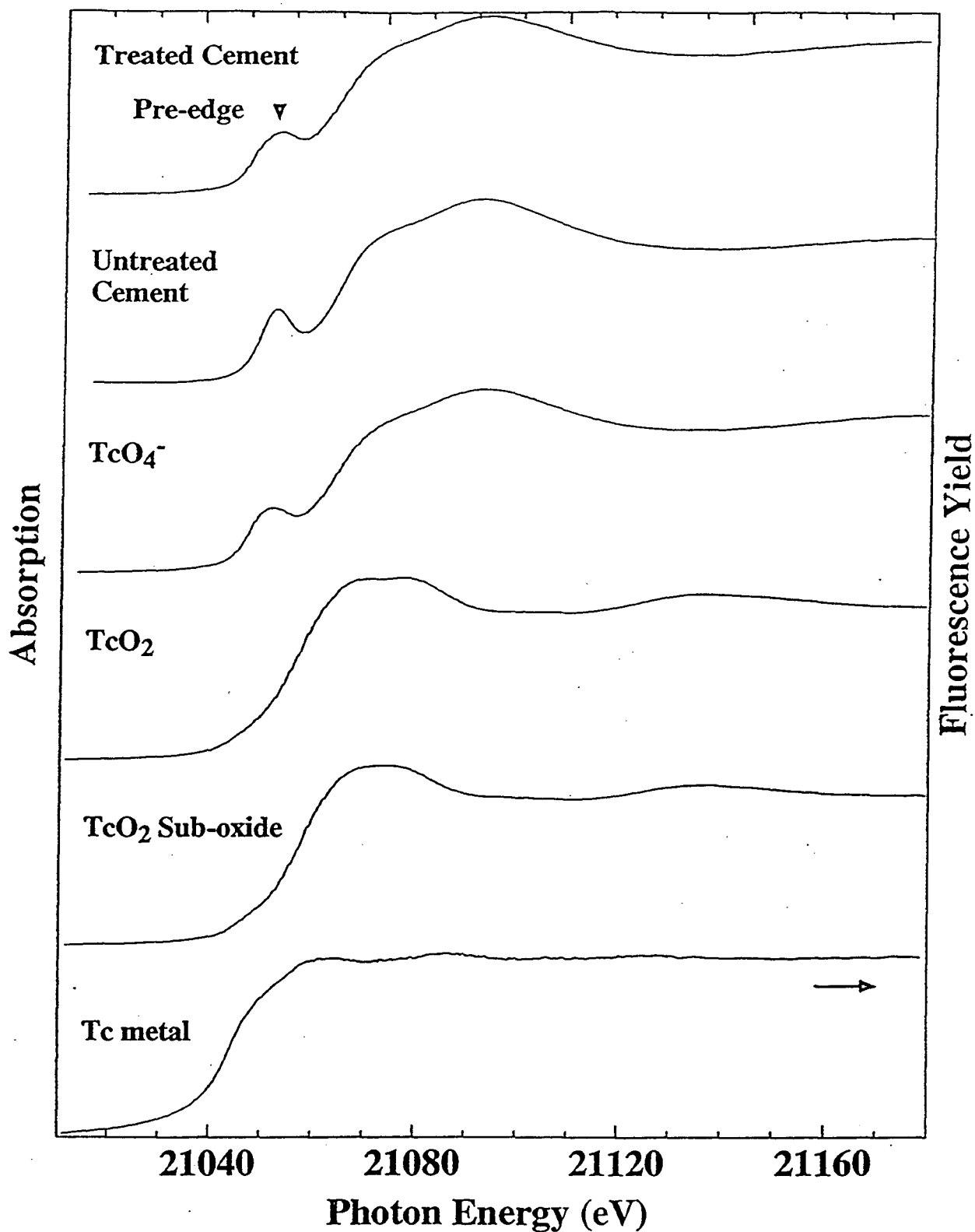


Figure 1. Technetium K edge XANES spectra from the treated and untreated Tc-containing cements, as well the Tc reference materials. The pre-edge feature, indicative of the tetrahedral coordination of the  $TcO_4^-$  species, is clearly evident. The spectra have been normalized and aligned with respect to the Tc metal edge at 21,044 eV.

spectra of the Tc-containing cements and the Tc reference materials (Tc metal,  $\text{TcO}_2(\text{IV})$ , and a  $\text{TcO}_4^-$ (VII) solution) are presented in Fig. 1. The range of chemical shifts for the Tc K edge has been characterized for the first time and spans  $\sim 20$  eV between the metallic and the  $\text{Tc}^{7+}$  state. The chemical shift from  $\text{TcO}_4^-$ (VII) to tetravalent  $\text{TcO}_2(\text{IV})$  is  $\sim 7$  eV, therefore resolving the difference in oxidation state solely on the basis of edge position is quite straightforward. Additionally, there is a characteristic pre-edge feature present in the  $\text{TcO}_4^-$  spectra that clearly fingerprints the tetrahedral  $\text{TcO}_4^-$  moiety.<sup>2,5-6</sup> The spectra of Tc metal and  $\text{TcO}_2$  have no such pre-edge features and exhibit edge positions significantly shifted to lower binding energies from that of  $\text{TcO}_4^-$ . Comparison of the XANES spectra of Tc in untreated cement to Tc in slag treated cement, shows that the primary oxidation state of Tc is the same in both cements since both display the distinctive pre-edge signature and have the same edge positions. Several locations within the treated cement were characterized and the results were the same throughout. Thus, the addition of slag to the cement formulation does not significantly reduce the  $\text{TcO}_4^-$  to  $\text{TcO}_2$  (or any other  $\text{Tc}^{4+}$  compound) in the cement samples examined in this investigation. The same cement samples were re-examined several months later employing the same experimental techniques and the results were duplicated exactly. Additionally, the analysis of the EXAFS from the Tc metal and  $\text{TcO}_2$  provides some of the first detailed structural information about these materials.<sup>7</sup>

### Speciation of Se After Bacterial Uptake

The concentration and stabilization of hazardous materials by microbial agents offers great potential for use in environmental remediation technologies.<sup>8-10</sup> Possible applications of bioremediation technologies are to oil refinery waste streams containing selenite and to the severely Se contaminated site at the Kesterson Reservoir in California. The aerobic soil bacterium, *B. subtilis*, is known to incorporate Se within or on the vegetative cell wall, although the exact mechanism of uptake is not fully understood.<sup>11</sup> The Se appears to be reduced and bound as red elemental Se, although there is no rigorous spectroscopic evidence to support this contention. The elucidation of the microbial mechanisms responsible for effective bioremediation will lead to improved bioremediation technologies.

The *in-situ* analysis of selenium following uptake by common soil bacteria *B. subtilis* and the Kesterson bacillus has been investigated by XANES, to elucidate the speciation of the Se contaminant in the biomass. The oxidation state of Se in the bacteria were determined by the chemical shifts at the Se K edge in comparison to those of the Se reference materials. Fig. 2 presents the Se K edge XANES spectra from the well-defined oxidation states of elemental Se (red and grey allotropes), a  $\text{Na}_2\text{SeO}_3$  powder, and a  $\text{Na}_2\text{SeO}_4$  powder. The chemical shifts at the Se K edge span  $\sim 9$  eV from the elemental allotropes of Se to the selenate(VI). There is a discernible difference between the red and grey allotropes of elemental Se in the near-edge region, even though the actual edge positions are indistinguishable. The structural differences are also clearly evident from the preliminary analysis of the EXAFS from these materials. The Se XANES spectra of the two bacteria are also shown after uptake of Se from a growth medium containing sodium selenite(IV) for comparison to that from the reference materials (Fig. 2). The spectra in Fig. 2 show that both *B. subtilis* and the Kesterson bacillus reduce the selenite to red elemental Se. This result is consistent with the conclusion that red elemental Se is the biologically active form.

## CONCLUSIONS

XANES techniques have been successfully employed to characterize the *in-situ* speciation of two hazardous environmental contaminants. A proposed chemical process to immobilize Tc in nuclear wasteform cements has been evaluated by XANES and there was no experimental evidence of a significant reduction of  $\text{TcO}_4^-$  to  $\text{TcO}_2$  (or any other  $\text{Tc}^{4+}$  compound). The complete range of the chemical shifts with oxidation state at the Tc K edge



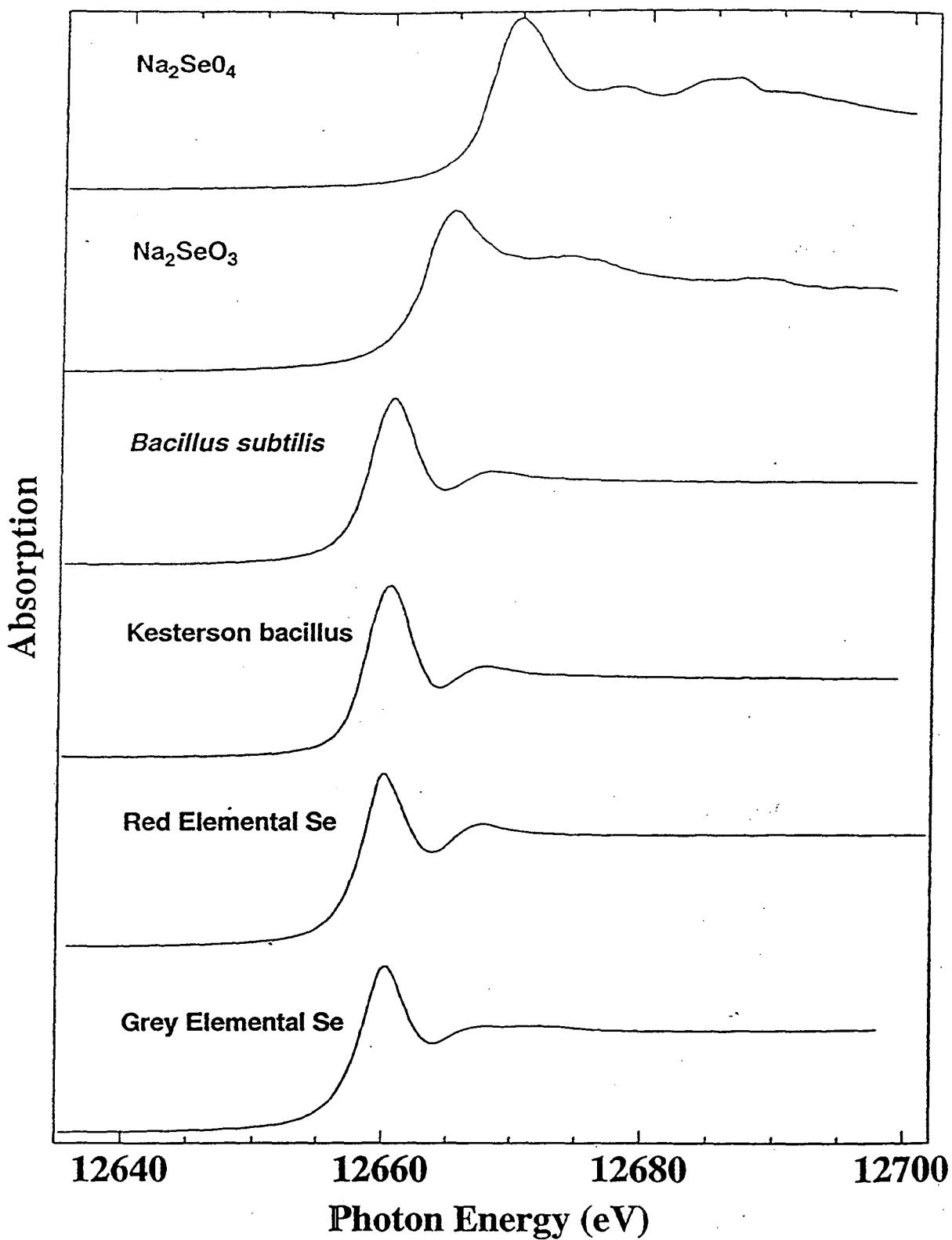


Figure 2. The Se K edge XANES spectra from *B. subtilis* and the Kesterson bacillus after growth in a selenite medium and the Se reference materials. The spectra have been normalized and aligned with respect to Se metal at 12,658 eV.

have been determined. The distinctive pre-edge signature of  $\text{TcO}_4^-$ , coupled with the chemical shift information, clearly differentiates it from the lower oxidation states of Tc.

The reduction of Se(IV) to red elemental Se by *B. subtilis* in culture has been documented by XANES and by comparison to known Se materials. The electronic and structural differences between the red and grey allotropes of elemental Se were found in the both XANES and EXAFS regions, respectively. The results support the view that organisms like *B. subtilis* offer a promising means for removing selenite (IV) from contaminated aqueous environments such as oil refinery waste streams. Future application of XANES techniques to the monitoring of *in-situ* selenium bioremediation activity is desirable.

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