

## VALENCE DISTRIBUTION OF As-76 ATOMS IN ARSENIC THIOCOMPOUNDS IRRADIATED WITH NEUTRONS

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**Abstract.** The distribution of the valence states III and V of radioactive  $^{76}\text{As}$  after neutron irradiations of thioarsenic compounds has been investigated. The irradiated compounds were thioarsenites as well as sodium thioarsenate; fresh precipitated arsenic trisulfide was also investigated. Materials were irradiated with neutrons at a flux of  $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ . The radioisotope formed by  $(n, \gamma)$  reaction is  $^{76}\text{As}$  with  $T_{1/2} = 26.4 \text{ h}$ . Separations of valence states were performed by high voltage electrophoresis at a gradient of  $35 \text{ V cm}^{-1}$  on 3MM Whatmann paper. Radiochemical yield of As(V) in the hydrated thioarsenites was very high but when dehydrated thioarsenite is irradiated, the yield of the radioactive As(V) was much lower and similar to that obtained in the irradiated disordered trisulfide. On irradiated thioarsenate the retention was also very high. These yields are like those found in the previous work on irradiating As sulfides and it seems to be related to the covalent character of the As-S bond; likewise, internal conversion accounts for the primary oxidation of recoil atoms.

**Keywords:** hot atom in solids, chemical changes, under neutron bombardment, arsenic thio compounds, optical electronic properties

### 1. INTRODUCTION

When an atom, in this case As, capture a particle, in this case a neutron, it emits  $\gamma$  rays and suffers a recoil: the reactions is:  $^{75}\text{As} (n, \gamma) ^{76}\text{As}$ . The recoil energy frequently is many times larger than the bonding energy of the atoms in the compounds, the bonding can be broken (Szilar-Charmes reaction) and different chemical processes are expected. If the processes occur into a solid-state system like, the recipient atom transmits energy to the neighbor and same time, and according the energy, the recoil atoms can jump from their sites with the production of colors centres, as well as, *inter alia*, ionization, lost/ capture of electrons, depending also of the structure. [1-5].

The distribution of valence states in radioactive atoms in irradiated arsenic sulfides indicated height yield of  $^{76}\text{As(V)}$  in comparison with the values obtained with arsenic oxides [6,7]. Arsenic sulfides, as well and antimony's and other thio-compounds are important components/materials of optical glasses according to their optical electronic properties [1- 5]. Under neutron bombardment they present changes in such properties as it happens, at very much lesser extent, when they are submitted *inter alia* to light or thermal induced processes [7]; and generate, therefore, chemical effects on the compounds as shown in the previous paper [8].

In this work, the studies are extended at some thio-salt and to disorders  $\text{As}_2\text{S}_3$ .

The final oxidation state of the irradiated/radioactive atom can be rich by internal conversion and or electron transfer. The first transition

between nuclear energy levels may be accomplished by the mechanism of internal conversion, and external nuclear electron, usually of K or L shell, may interact with nucleus being capture by the nucleus, leaving a hollow; then outer electron can jump into the hollow with de emission of X-ray. An electron cascade can be produced and in consequence, in the increase of the oxidation state. Electronic transfers can be produced in the solid state or in dissolution, conducive to changes of the oxidation state as mentioned above.

### 2. EXPERIMENTAL

#### 2.1. Materials

The irradiated materials were disordered  $\text{As}_2\text{S}_3$  fresh precipitated and thioalts of arsenic:  $\text{K}_3\text{AsS}_3$ ,  $\text{Na}_3\text{AsS}_3$ ;  $\text{Na}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$  and dehydrated  $\text{Na}_3\text{AsS}_3$  and  $\text{Na}_3\text{AsS}_4$  water soluble, prepared according conventional methods and procedures [9,10].

#### 2.2. Irradiations

Materials were irradiated in the RA3 research/production swimming pool reactor in the Atomic Center of Ezeiza - Argentina, with a flux of  $2 \times 10^{12} \text{ n cm}^{-2} \text{ seg}^{-1}$  under nitrogen or in evacuated ampoules. When arsenic compounds are irradiated with neutrons, the radioisotope  $^{76}\text{As}$  of known characteristics [11], is formed by  $(n, \gamma)$  reaction;  $^{76}\text{As}$  by  $\beta^-$  decay, originates stable  $^{76}\text{Se}$ .

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2.3. Analysis

As in the previous work [8], the procedure was as follows: the activated compounds were dissolved in 1.3% sodium sulfide solution in the presence of either, As(III) or As(V) carrier. The various valence states were separated by paper electrophoresis [12] using Whatman 3MM paper. The voltage gradient was 40V/cm and the electrolyte was a dissolution of 0.4% in Na<sub>2</sub>S and 0.04% in NaOH.

2.4. Measurements

The counting of the paper strips of 1 cm wide was carried out either with an end window GM counter or with a NaI (Tl) crystal.

3. RESULTS AND DISCUSSION

The distribution of valence states III & V of radioactive arsenic according their activities is breakdown in Table 1 (calculations in Excel 2016).

Table 1. Distribution of \*AsIII & \*AsV (%)

Compounds	As III %	As V %	Experiments (n)
As <sub>2</sub> S <sub>3</sub>	34.8± 3.39	63.4 ±6.86	(6)
Na <sub>3</sub> AsS <sub>3</sub>	37.6 ±4.0	63.0±7.62	(6)
K <sub>3</sub> AsS <sub>3</sub>	39.4±4.3	59.5±7-3	(6)
Na <sub>3</sub> AsS <sub>4</sub>	24.0±3.16	80±9.12	(6)
Na <sub>3</sub> AsS <sub>4</sub> ·8H <sub>2</sub> O	-	99.98± 0	(6)
Na <sub>3</sub> AsS <sub>3</sub> ·nH <sub>2</sub> O	41.8±6.14	56.2± 8.40	(4)

It shows that, in comparison with neutron irradiation of arsenic oxycompounds, the yield of the pentavalent form in the sulfides, is much higher than in the former. These results are similar with those obtained in the neutron irradiation of oxy and thio compounds of antimony [13,14]. Such an effect is considered to be related to the covalent character of the Sb-S and As-S bonds; as well to the internal conversion oxidative effects to electronic transfer in the lattice upon irradiation [8,15 ,16].

In the nuclear process <sup>75</sup>As (n,γ) <sup>76</sup>As the prompt γ spectrum is very complex and broad; the number of gamma being N γ =348 with a wide de-excitation energy photons distribution: extended from 44.42 to 7284.07 KeV[17]; most intense of 559.10, 165.049, 86.788 KeV. Then the recoil atoms energy spectrum must also be broad and most of them cannot travel far in the solid before resting, but only a few inter atomic distance in the lattice. The more energetic atoms transfer their energy into the lattice and could produce the ejection of some other atoms in the thioarsenic compound structure [17] originating cationic vacancies “incipient V centres” [15] but most of them produce in the host atoms electronic excitation, vacancy cascades, ionizations as well as changes in the As<sub>2</sub>S<sub>3</sub> bandgap.

Also, it has been observed that when amorphous non irradiated As<sub>2</sub>S<sub>3</sub>, according to reference [18] is annealed at the glass-transition temperature, i.e., heated to increase the energy, the medium-range order may develop or increase, lessening the covalent bonding character and rising the chemical order [18].

In regard to the pentasulfide As<sub>2</sub>S<sub>5</sub>, its structure is unknown though from the study of amorphous variety, the short/middle range order is similar to that of amorphous As<sub>2</sub>S<sub>3</sub>, but the structure of As<sub>2</sub>S<sub>5</sub> is more

rigid [19], and in it, in some cluster present As<sub>2</sub>S<sub>5</sub>, As<sub>4</sub>S<sub>6</sub>, As<sub>6</sub>S<sub>9</sub>. [4] have been identified.

In this regard, two different samples of As<sub>2</sub>S<sub>3</sub> were submitted to neutron bombardment. One of them ordered, as described above; the other, disordered freshly precipitated. The retention \*As(III), at t = 0 was higher in the disorder, 37.4% vs 28.4% in the commercial sample as described elsewhere [8]; in addition the disorder rich the final valence state faster than in the structured sample.

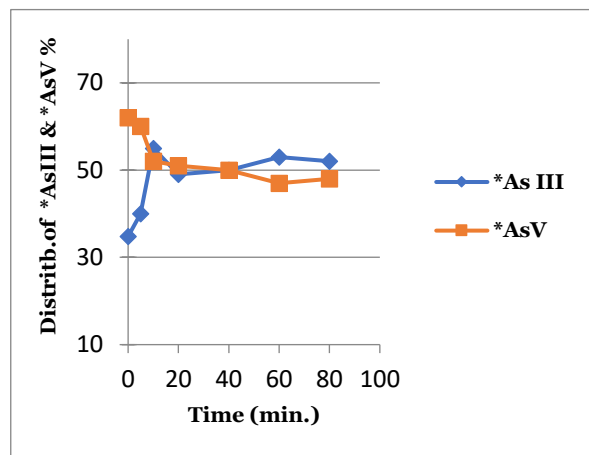


Figure 1. Annealing of disordered arsenic trisulfide (80°C)

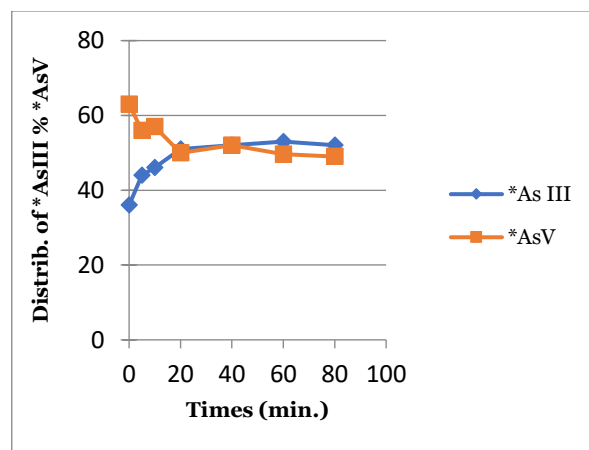


Figure 2. Annealing of sodium thioarsenite (80°C)

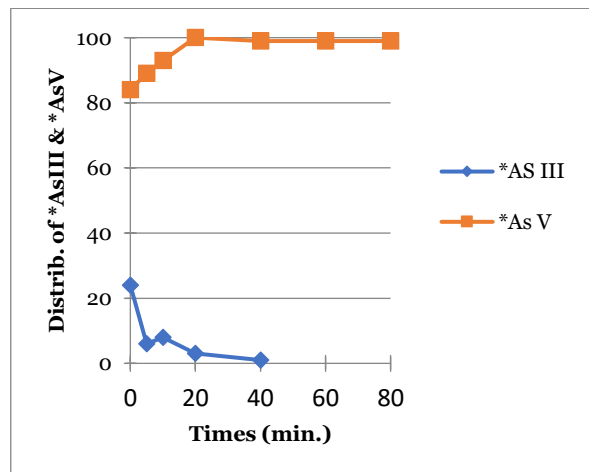


Figure 3. Annealing of sodium thioarsenate (80°C)

The yield of As(V) in the thioarsenites is higher than in the ordered trisulfides but close to that found in the disordered sulfide. Besides, in the hydrated thioarsenite, the yield is even much higher. The origin of these species must be a reaction of the water with primary recoil fragments or exchange reactions between sulfur and oxygen atoms or OH groups.

In this regard, the chemical changes in the irradiated arsenic thio-compounds, internal conversion (IC) phenomena should occur in huge number [20] generating vacancies cascades and producing a large amount of free electrons, that is, a reductive ambience for the recoil/excited atoms and ions, as well as the formation of F centers, reduction of V centers etc. On irradiated As<sub>2</sub>S<sub>3</sub>, As(IV) hot atoms could result by IC, which dismutate in \*As (III) and \*As (V) species, as discussed in detail elsewhere [8] and here suggested in (Fig.3); similar result and mechanism on the formation of \*Sb (III) hot atoms were observed in the neutron irradiation of Sb<sub>2</sub>S<sub>3</sub> [13-14]

Annealing experiments, carried out at 80 ± 1°C were performed on samples of disordered As<sub>2</sub>S<sub>3</sub>, (Fig. 1) Na<sub>3</sub>AsS<sub>3</sub> (Fig.2) and Na<sub>3</sub>As<sub>3</sub>S<sub>4</sub> (Fig.3), as shown below, confirm that of above exposed as it is shown in Fig 1. It also shows that the \*As(III) reached its final state at the end or in a short lapse after irradiation.

#### 4. CONCLUSION

The higher yields of radioactive As(V) in the sulfides, as compared to the oxides, can be attributed to the type of structure and to the higher covalent character of the As-S bond as well as oxidation reaction promoted by IC and electron transfer.

Under annealing, disordered irradiated As<sub>2</sub>S<sub>3</sub> show an increase of \*As(V) formation, in comparison of ordered trisulfide more compact with high bonding energy in its their layer structure. In the arsenite and the trisulfides, the \*As(V) atoms are reduced to \*As(III) by the large availability of electrons and F centers decreasing the yield of the former and increasing that of the latter; the final yield is reached a few minutes after the end of irradiation; in sodium thioarsenite the retention is close to that of the disordered under annealing the changes upon time show differences that must be to the effects of water molecules.

In Na<sub>3</sub>AsS<sub>4</sub> the retention is ~ 100% and the hot-atoms reach their final state during or immediately at the end of irradiations. This oxidation occurs faster in the hydrated thioarsenate.

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