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## **STUDYING THE EFFECT OF USING DIFFERENT STABILIZERS ON THE STABILITY OF SILVER STANNATE $Ag_2SnO_3$**

*Аннотация:* В этом исследовании мы изучали стабильность геля, который используется для приготовления станната серебра  $Ag_2SnO_3$  методом «золь-гель обработки». Были изучены эффективные условия процесса приготовления геля (тип стабилизатора, молярное соотношение: (стабилизатор: смешанные оксиды), время, температура и т.д.), И оптимальные условия для достижения наилучшей стабильности полученного геля были определяются. В ходе этого исследования мы обнаружили, что использование  $\beta$ -каррагенана в качестве стабилизатора со стабилизатором молярного соотношения: смешанные оксиды (0,085: 1) в течение трех дней при комнатной температуре доказало лучшую стабильность для геля.

*Ключевые слова:* Соль-гель, смешанные оксиды, Серебряный Стантес,  $\beta$ -каррагинан.

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## **1. Introduction:**

A lot of chemical methods of preparing so many mixed oxides had been used by the researchers; such as Solid-State Synthesis, Co-precipitation, Hydrothermal method and Sol-Gel method in addition. All of these methods depends on experimental different processors.

### **1.1. Solid-State Synthesis:**

The principle of this method is based on mixing the used oxides to prepare the network according to their stoichiometric ratio in the presence of acetone, the samples grind well to ensure the greatest homogeneity of these oxides. The process is repeated more than once to ensure more homogeneity. Then the mix of the oxides is pressed to form tablets by using a piston with high compression capacity. It is then calcified at the appropriate temperature to synthesize each mixed oxides compound.

The advantages of this method are: there simplicity and ease of use, besides the no need of using complicated equipment, Moreover, the effective conditions on forming the network are limited by homogeneity amount, temperature and time of calcification.

Meanwhile, the disadvantages are: not obtaining a homogeneous mixture of the oxides due to the mechanical mixing which is done by the researcher, besides the high required temperature for preparing the network and the reaction that take place between oxides. As it doesn't give high yields of the prepared networks due to the large proportion of the non-reacted oxides. [1]

### **1.2. Co-Precipitation Method:**

In this method, solutions of the metal salts which exist in the structure of the wanted compound are prepared, and it is added by slow distillation into a basic solution of ammonium hydroxide or sodium hydroxide which is equipped with a magnetic stirrer.

When the salts solutions are added to the basic solution, the metal hydroxides are formed, In the presence of stirring and slow addition, a greater dispersion and homogeneity occurs for the combination of these hydroxides, after addition, the hydroxides are separated by filtration, dried and calcified at the appropriate temperature to synthesize the desired mixed oxides compound.

The advantages of this method are the occurrence of greater homogeneity than the Solid-State Synthesis besides the ease application of this method.

Meanwhile, the disadvantages are: the effect of the basic solution pH value on the hydroxide precipitation process, where some of the metal hydroxides are formed only with a medium of appropriate pH and therefore not suitable for all types of the mixed oxides compounds, the first metal hydroxide might be formed but the second might not, beside the high temperature that required to make the reaction between the mixed hydroxides to form the desired compound, especially that the reaction is two-step: at first the metal oxides are formed, second these oxides are reacted with each other to form the compound. Thus, the second step of the reaction is similar to the method of the Solid-State Synthesis we talked about previously. [2]

### **1.3. The Hydrothermal Method:**

The principle of this method is based on preparing the desired metal salts and then putting them at an autoclave made of resistant and chemically inactive Teflon, they are placed at a certain temperature for a period of time (12 hours) where the desired oxides are formed. The oxides are separated, washed and calcified at the appropriate temperature to synthesize the desired compound.

The advantage of this method is the preparation of a homogeneous mixture of the oxides with a very small crystallization volume.

Meanwhile, the disadvantages are the very long time that is required to form the oxides adds to the high pressure where is resulted inside the autoclave which might cause an explosion in some cases. [2]

#### 1.4. Sol-Gel Method:

Although this method was discovered about 200 years ago, it has taken place in the industry since the sixties of the last century and has been increasingly used in recent years for its advantages that traditional methods of synthesis do not have. [3]

This method is directed to the formation of inorganic oxides with gel structure, which can be defined from the thermodynamic point of view as relatively stable solid phase formation at a certain temperature, starting with the liquid phase (the solvent).

By this method, certain materials with unique and desired applied properties can be obtained, such as mechanical hardness, photovoltaic permeability, chemical stability, porosity with required dimensions (can be controlled by request), etc. [4]

In order to identify the sol-gel method, we first need to define the types of solutions [5] according to the dimensions of the dissolved materials:

**Real Solution:** The dimensions of the dissolved material are often small in size, such as simple sugars, acids and simple bases with a low molecular weight (not large dimensions), so there are no separation surfaces between the solvent material and the dissolved material can be observed and the solution is homogeneous and transparent.

**Suspension Solution:** The particle's dimensions are bigger than 1000 Å, such as the insoluble salts in water.

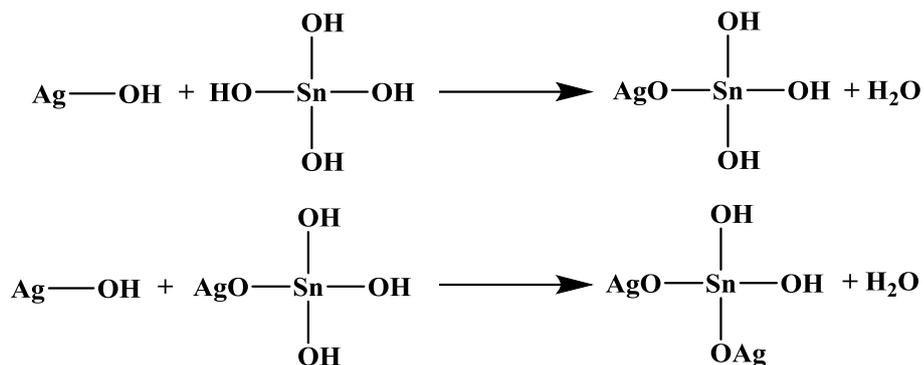
**Colloidal Solution:** The dissolved material is a huge molecule, ranging from 10-1000 Å, such as biologic and synthetic polymers and some inorganic acid salts, one of the advantages of this solution is its diffusion of visible light, known as Sol, which is what we are interested in our study.

Thus, this method is based on the preparation of Sol solutions for the metal salts in the structure of the network and then mixing them and leaving them to form the gel, after this they are separated and washed, then they are calcified at the appropriate temperature. The following processes describe the steps in detail:

- A. **Hydrolysis:** At this stage, the metal salts are hydrolyzed by solving them in water in the presence of a basic solution of ammonium hydroxide, where the required metal hydroxides are formed.

**B. The formation and growth of the gel:** here, the hydroxides are mixed with each other in the presence of a stability factor (stabilizer), which prevents the metal hydroxides from precipitation and forms the stable colloidal solution. At this stage, the condensation process (polymerization) of the hydroxides is happened and begun to conjugate with each other to form a three-dimensional network of the conjugated metal hydroxides chains.

The following scheme.1 shows the conjugation process between the hydroxides:



**Scheme 1.** the conjugation process between the hydroxides.

And this is the beginning of gel formation. Over time, the gel continues to grow and the length of polymer chains is increased and extended in all directions. This process is called "Ageing". The gel becomes more stable and its crystals become more homogenous.

**C. The Drying Process:** in this stage, the formed gel is separated by filtration, washed by distilled water and dried at the appropriate temperature (it is often about 105 °C) for aqueous solutions.

It must be noted that The Drying Process has the main role in determining the physical and structural properties of the resulting compound. At normal drying, some molecules of the solvent are faded away from within the formed gel's pores, and as a result to the huge surface tension forces of water molecules, the pores collapse and the density of the resulting material increases, this state is called "Xerogel".

In order to reduce the surface tension and prevent the pore collapse, the researchers have developed a number of drying methods, including:

- **Solvent Replacement Method:** here, the original solvent (usually water) is replaced by another solvent with less surface tension force (like ethanol), where the gel is soaked

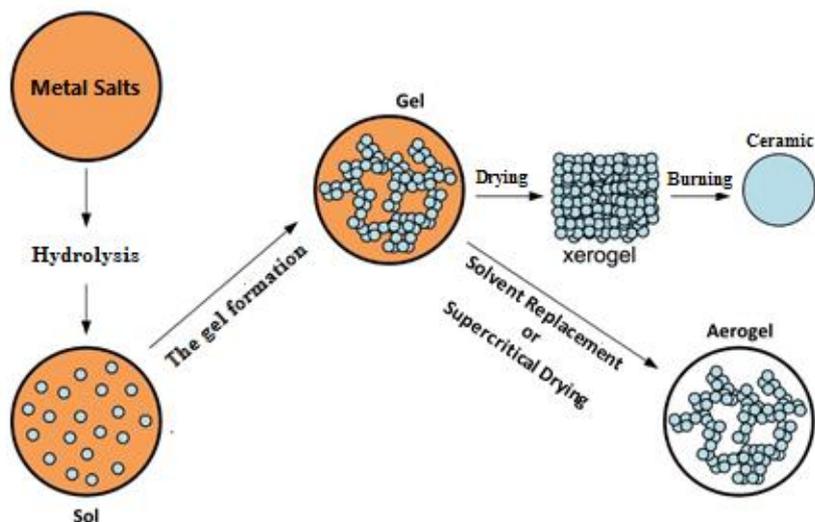
with water-ethanol solution (9-1 percent), then washed by the same solution and transferred to another water-ethanol solution (8-2 percent), the process goes on until the absolute ethanol solution is reached. Then the ethanol is replaced by hexane in the same way, as hexane has a very low surface tension force and doesn't affect the pores during the drying process, but it can't be replaced directly at first replacement because it doesn't mix with water.

- **Supercritical Drying:** it is done under the high pressure of carbon dioxide ( $\text{CO}_2$ ), where the water is replaced by  $\text{CO}_2$ , then the applied pressure is reduced gradually which allows to the gas ( $\text{CO}_2$ ) to leave the pores.

The methods of drying as mentioned above affect the structure of the resulting compound. The methods of replacing the solvent and Supercritical Drying is used to obtain a material with low density, high porosity, and a large qualitative surface. the produced materials in this state are called "Aerogel".

This is one of the most important benefits of the Sol-gel method, which allows obtaining different types and structures of the same material by changing the drying method only.

- D. The Burning Process:** here, the produced samples from the drying process are burned under the appropriate temperature to synthesize the mixed oxides compound, and what is worth to mention, That the required temperature here is much lower than the needed one in preparing the mixed oxides compound by other methods, as the hydroxides are linked to each other in the (sol-gel) method, while the method of the Solid-State Synthesis, for example, is required a very high temperature so the reaction between the mixed oxides can be obtained.



**Figure 1.** shows Sol-Gel Preparation Stages.

The most sensitive stage in the preparation process is the gel formation, Therefore, many researchers had studied the use of different stabilizers and studied the effective factors on them to obtain the best stability.

The researcher Ismaeel et al. had used acid vinegar as a stabilizer in the process of preparing the compound, Zen Al-Abedin et al. also used acetic acid, Other researchers have used many chemicals, especially organic ones, as stabilizers, including TEOS, TMOS [6], methanol, 1-propanol, 2-propanol, 1-butanol, ethylene glycol [7].

The aim of this research is to study the use of several new stabilizers not previously used in the preparation of  $\text{Ag}_2\text{SnO}_3$  and the factors affecting their stability.

## 2. Experimental:

### 2.1. Materials:

Silver nitrate 99.8% ( $\text{AgNO}_3$ ) was purchased by (Riedel deHaen).

Tin (IV) chloride pentahydrate 98% ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ),  $\beta$ -carragenan ( $\text{C}_{24}\text{H}_{38}\text{O}_{19}$ ) were purchased by (Sigma-Alrich).

Ammonium hydroxide % was purchased by () .

### 2.2. The Apparatus and Instruments Used:

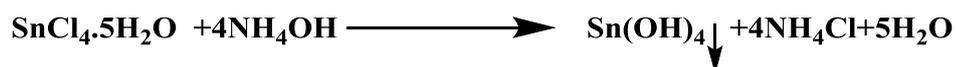
Analytical balance with accuracy up to 0.0001 gr. Different glass tools. A ceramic crucible with temperatures up to 1100 °C. A dryer for drying the samples from Memmert company. An incinerator for burning samples with temperatures up to 1100

°C from Carbolite company. A ceramic mortar to grind the samples and get a fine powder as possible.

### 2.3. Synthesis:

#### 2.3.1. Preparation of Tin(IV) Hydroxide Sn(OH)<sub>4</sub>:

Tin(IV) Hydroxide was prepared from Tin (IV) chloride pentahydrate salt, Tin (IV) chloride pentahydrate (0.014 mol, 5 gr) was mixed with Ammonium Hydroxide (0.056 mol, 8.6 mL), according to scheme 2:

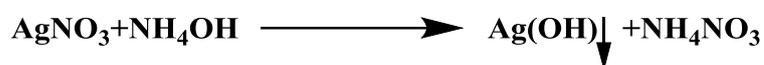


**Scheme 2.** Preparation of Tin(IV) Hydroxide Sn(OH)<sub>2</sub>.

A white precipitate of Tin(IV) Hydroxide was formed and separated by filtration, then washed several times with distilled water to remove the suspended chlorine ions, where the chlorine ions were detected by examining the filtered solution with silver nitrate.

#### 2.3.2. Preparation of Silver Hydroxide AgOH:

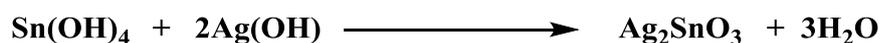
Silver Hydroxide was prepared from Silver nitrate salt, Silver nitrate (0.028 mol, 4.76 gr) was mixed with Ammonium Hydroxide (0.028 mol, 4.3 mL), according to scheme3:



**Scheme 3.** Preparation of Silver Hydroxide AgOH.

A brown precipitate of Silver Hydroxide was formed and separated by filtration, then washed several times with distilled water.

The prepared hydroxides were mixed with a molar ratio (2:1) of Silver hydroxide and Tin (IV) hydroxide, respectively, which is the right accounted ratio to form Silver stannate (Ag<sub>2</sub>SnO<sub>3</sub>) based on scheme 4:

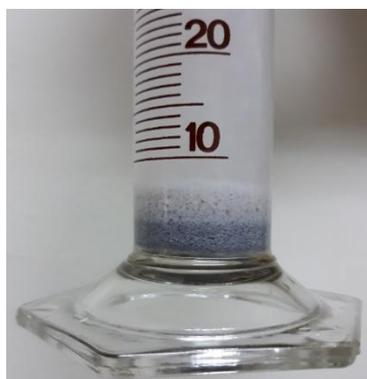


**Scheme 4.** Preparation of Silver stannate (Ag<sub>2</sub>SnO<sub>3</sub>).

### 3. Result and discussion:

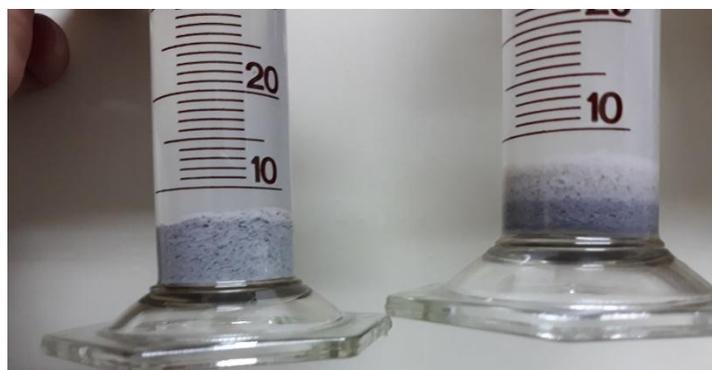
#### 3.1. The Importance of Using the Stabilizers in The Preparation of Silver Stannate (Ag<sub>2</sub>SnO<sub>3</sub>):

When Silver hydroxide and Tin (IV) hydroxide were mixed according to previous molar ratio (2:1) with (100 mL) distilled water without adding the stabilizer, a direct precipitation of the hydroxides was observed, where Silver hydroxide was precipitated first as brownish layer, and above it a white layer of Tin (IV) hydroxide depending on their density as shown in figure 2:



**Figure 2.** The precipitated layers of Silver hydroxide and Tin (IV) hydroxide.

And according to the previous observing, it was showed the necessary existence of the stabilizer to ensure the homogeneity first and then the stability of the prepared Silver Stannate ( $\text{Ag}_2\text{SnO}_3$ ), figure 3. Shows the homogeneity in the case of the stabilizer presence compared to the previous case of the stabilizer absence.



**Figure 3.** A comparison between the stabilizer presence and the stabilizer absence.

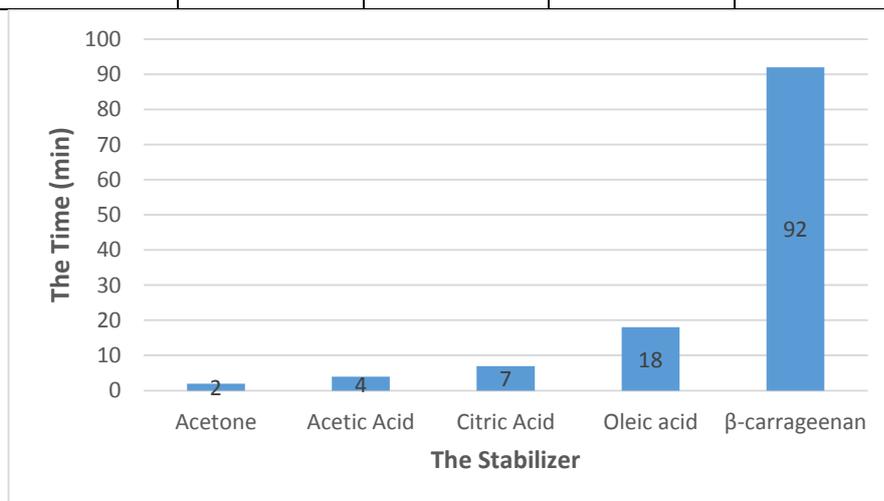
In order to choose the best stabilizer to reach the stability of the prepared Silver Stannate ( $\text{Ag}_2\text{SnO}_3$ ), we have studied the relation between stabilizer type and the required time to the separation process:

The prepared Tin (IV) hydroxide was mixed with Silver hydroxide after adding (100 mL) distilled water, the mixture was stirred for two hours at room temperature until obtaining complete homogeneity, then was distributed on five graduated cylinders with a capacity of (20 mL). Then an equivalent quantity of the stabilizer was added (10 mL)

to the constant quantity of the prepared Silver Stannate ( $\text{Ag}_2\text{SnO}_3$ ), the samples were monitored to choose the best stabilizer for the stability of the prepared Silver Stannate ( $\text{Ag}_2\text{SnO}_3$ ). The best stabilizer was chosen, which had achieved the longest period of time to stabilize the formed compound, and it's  $\beta$ -carrageenan.

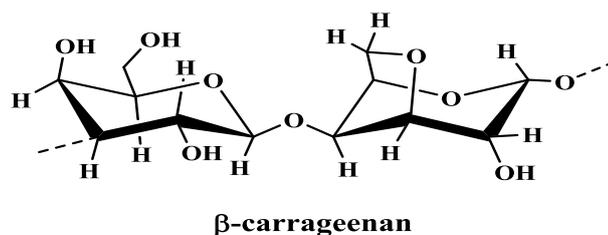
Table 1. the relation between stabilizer type and the required time of the separation process:

Stabilizer Type	Acetone	Acetic Acid	Citric Acid	Oleic acid	$\beta$ -carrageenan
The Added Quantity	10 mL	10 mL	10 mL	10 mL	10 mL
The Time (min)	2	4	7	18	92



**Figure 4.** the relation between stabilizer type and the required time to the separation process.

$\beta$ -carrageenan is a natural organic polymer product and has the following structure:



**Figure 5.** the structural formula of  $\beta$ -carrageenan.

And it is one of the most important stabilizing factors that used in food and chemical industries and the preparation of a high stability gels, it has a total formula  $C_{24}H_{38}O_{19}$  and molecular weight 630 gr/mol. [8]

### 3.2. Studying The Effect of the Stabilizer Amount on The Prepared Silver Stannate:

The solution of the hydroxides was prepared the same way, then was distributed on five graduated cylinders with a capacity of (20 mL), each cylinder contains 0.0028 mol of Tin (IV) hydroxide and 0.0056 mol from Silver hydroxide, Incremental quantities of the stabilizer have been added and its consistency has been monitored over time. The obtained results are shown in the following table:

**Table 2.** the effect of the stabilizer amount on the Silver Stannate ( $Ag_2SnO_3$ ).

Gram Amount Of The Stabilizer (gr)	Molar Amount Of The Stabilizer (mol)	Molar Amount Of Silver Hydroxide (mol)	Molar Amount Of Tin (IV) Hydroxide (mol)	The Time Of The Stability (min)
0.05	$7.93 \times 10^{-5}$	0.0056	0.0028	21
0.075	$1.19 \times 10^{-4}$	0.0056	0.0028	39
0.1	$1.58 \times 10^{-4}$	0.0056	0.0028	92
0.125	$1.98 \times 10^{-4}$	0.0056	0.0028	176
0.15	$2.38 \times 10^{-4}$	0.0056	0.0028	215
0.175	$2.77 \times 10^{-4}$	0.0056	0.0028	234
0.2	$3.17 \times 10^{-4}$	0.0056	0.0028	251

In order to determine the molar ratio of the three components (tin (IV) hydroxide, silver hydroxide, stabilizer), we divide the molar number of each one by the smallest molar number (0.0028), as follows:

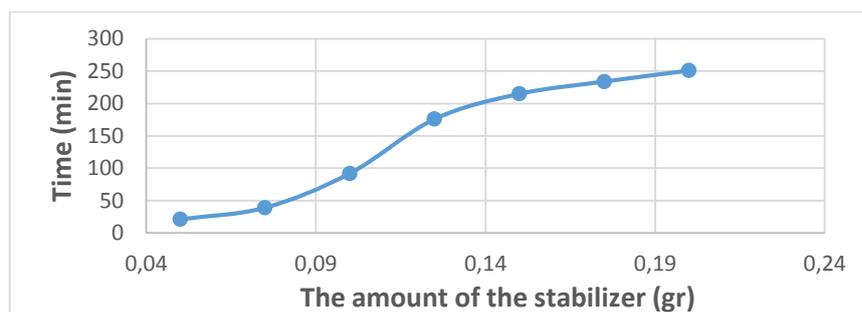
**Table 3.** the molar ratio of tin (IV) hydroxide, silver hydroxide, and stabilizer.

Gram Amount Of The Stabilizer (gr)	Molar Ratios			The Time Of The Stability (min)
	Stabilizer	Silver Hydroxide	Tin (Iv) Hydroxide	
0.05	0.0283	1	2	21
0.075	0.0425	1	2	39
0.1	0.0567	1	2	92
0.125	0.0709	1	2	176
0.15	0.085	1	2	215
0.175	0.0992	1	2	234
0.2	0.1134	1	2	251

**Table 4.** the molar ratio of the stabilizer and the prepared Silver Stannate ( $\text{Ag}_2\text{SnO}_3$ ).

Gram Amount Of The Stabilizer (gr)	Molar Ratios		The Time Of The Stability (min)
	Stabilizer	The Prepared Silver Stannate ( $\text{Ag}_2\text{SnO}_3$ )	
0.05	0.0283	1	21
0.075	0.0425	1	39
0.1	0.0567	1	92
0.125	0.0709	1	176
0.15	0.085	1	215
0.175	0.0992	1	234
0.2	0.1134	1	251

The chart of stability time as a function of the added amount of the stabilizer is shown in figure 6:



**Figure 6.** the stability time as a function of the added amount of the stabilizer.

From the chart, we had noticed that the stability of the prepared Silver Stannate ( $\text{Ag}_2\text{SnO}_3$ ) is increased by increasing the amount of the stabilizer, ie, there is a direct correlation proportionality between the stability of the prepared Silver Stannate ( $\text{Ag}_2\text{SnO}_3$ ) and the quantity of the added stabilizer. In this research, we had adopted a quantity of the stabilizer (0.085 mol).

### 3.3. Studying the Stability of the Prepared Silver Stannate over Time in the Presence of $\beta$ -carrageenan Stabilizer:

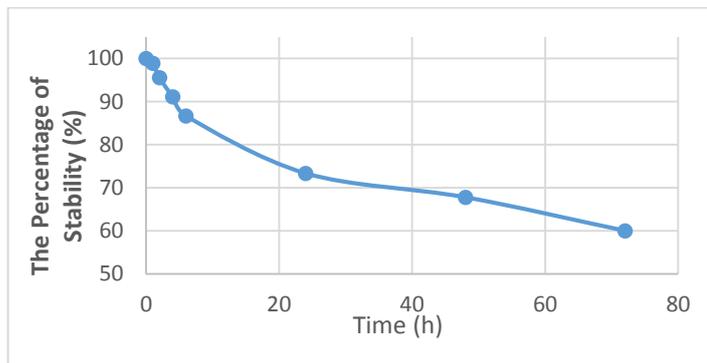
The solution of Silver stannate was prepared with a molar ratio (2:1:0.085) of Silver hydroxide, Tin (IV) hydroxide, and  $\beta$ -carrageenan, respectively, the stability of the solution was monitored over time. The obtained results are shown in the following table:

**Table 5.** the stability of the prepared silver stannate over time in the presence of  $\beta$ -carrageenan.

The Stable Amount (gr)	The Percentage of Stability (%)	Time (h)
90	100	0
89	98.88	1
86	95.55	2
82	91.11	4
78	86.66	6
66	73.33	24

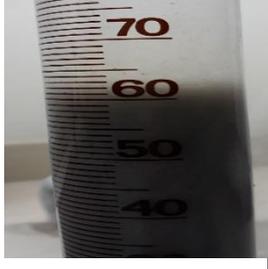
61	67.77	48
54	60	72

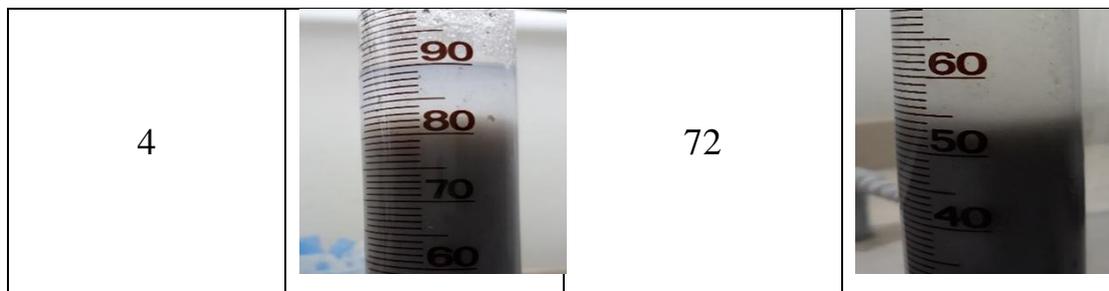
The chart of the percentage of stability as a function of time is shown in figure 6:



**Figure 7.** The Percentage of Stability as a function of time.

**Table 6.** shows the decrease in the stability of the prepared Silver Stannate over time.

Time (h)	The Stable Gel State	Time (h)	The Stable Gel State
0		6	
1		24	
2		48	



The prepared silver stannate was observed for more than four days, the gel had started to enter a new stage of instability, where the stable size wasn't decreased. But, a lot of holes were started to appear through the stable gel as it is shown in figure 8.



**Figure 8.** the formed holes through the stable gel after three days.

After observation, we had found that three days is the best time for gel formation and growth.

### **3.4. Studying the relation between the stability of the Prepared Silver Stannate and Temperature Degree:**

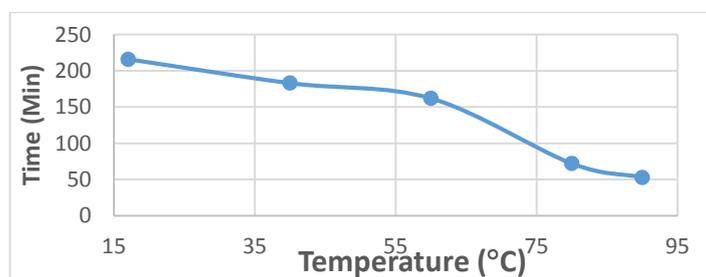
The Silver Stannate was prepared according to the previously mentioned molar ratio, in the same way, it was stirred to ensure homogeneity and was placed in a cylinder inside a water bath at room temperature (17 °C).

The experiment was repeated on different water bath's temperature degrees, to study the effect of the temperature on the stability of the prepared Silver Stannate. The obtained results are shown in the following table:

**Table 7.** shows the required time of each temperature.

<b>Temperature (°C)</b>	<b>Time (Min)</b>
17	216
40	183
60	162
80	72
90	53

The chart of time as a function of temperature is shown in figure 7:



**Figure 9.** the decrease in the stability of silver stannate with a temperature rising.

From the chart, we had observed a slight decrease in the stability when the temperature was raised from (17) to (60) and a sharp decrease when the temperature was raised from (60) to (80). This is due to the physical phenomena affecting the stability of colloid particles, As the temperature increases, the thermal (Brownian) motion of the stationary particles increases and the collision rate increases with each other. So It bounds and lumped with each other and its weight increases and thus begins to precipitate and lose the stability. Thus, the higher the temperature the less the stability of the silver stannate. The experiment is shown in figure 10:



**Figure 10.** the temperature effect on silver stannate stability.

#### 4. Conclusions:

- Several stabilizers were used in the preparation process of  $\text{Ag}_2\text{SnO}_3$ ,  $\beta$ -carrageenan was the best stabilizer.
- The optimal conditions were studied such as molar ratio, time and temperature. It was observed that the prepared silver stannate is highly stable at the first three days, and then it becomes lumpy and loses its stability and homogeneity.
- It was also observed that the stability of the prepared silver stannate and its mass was reduced by raising the temperature.

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