

# ASSESSMENT ON THE RATE OF EFFECTIVENESS OF POLLUTANTS SCAVENGERS ON HYDROGEN SULPHIDE

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## Introduction

Hydrogen sulphide is a commonly known pollutant to museums with silver collections. The effects and degradation of hydrogen sulphide (H<sub>2</sub>S) to silver is also widely studied. A lowest observed adverse effect dose (LOAED) as little as 2.5 ppb per year (or 3.85 µg per m<sup>3</sup> per year) of exposure to H<sub>2</sub>S could result in visible tarnish on silver (Ankersmit, 2005). There are various techniques employed by different museums to reduce the rate of corrosion to silver objects on display as well as in storage. One of the techniques is the use of pollutant scavengers to absorb the identified source of pollutants that harm silver. The study project specifically aims to ascertain the effectiveness of self-made sorbent H<sub>2</sub>S scavenger along with other commercially available scavengers.

## 1 Objectives and rationale of the study project

- 1.1 To investigate and compare the rate of effectiveness of selected pollutant scavengers that could exhaust H<sub>2</sub>S. The self-made sorbent scavenger is based on zinc carbonate (ZnCO<sub>3</sub>) solution applied on acid-free blotter. Its effectiveness is benchmarked against the sulphur scavenging product for preservation purpose Miracle Sac™ by Icel Developments Ltd, UK. It is not the desire of this study project to test on preservation products that are known to reduce rate of tarnishing on silver.
- 1.2 To execute the investigation in 2 phases. The first experiment was conducted over a span of 3 months from 30 August 2007 to 3 Dec 2007 and the other conducted over a span of 16 months from 23 April 2008 to 14 Aug 2009. The second experiment was an improvement of the first after evaluation was made on the scavengers, setup, and process of the test and hence ran for a longer duration to provide a clearer assessment of the scavengers. In the first experiment, other than the self-made scavenger, zinc carbonate powder itself is also used as scavenger but without a sorbent, such as acid-free blotter. In the second experiment, this was replaced with Seachem's Matrix Carbon™, an activated carbon designed to filter organic matter in water.
- 1.3 To investigate and compare the rate of effectiveness of selected pollutant scavengers that could exhaust H<sub>2</sub>S based on 4 most possible environments a silver object could be exposed to:
  - 1.3.1 An open and uncontrolled environment with higher level of H<sub>2</sub>S
  - 1.3.2 An enclosed environment with lower level of H<sub>2</sub>S, eg. Air-conditioned office
  - 1.3.3 Museum environment but low relative humidity (<55%RH) and high level of H<sub>2</sub>S
  - 1.3.4 Museum environment (55 – 65%RH) with high level of H<sub>2</sub>S

- 1.4 To incorporate control to each of the environment in order to understand the level of tarnish achievable on the silver coupon **without the use of scavengers** and thereafter in comparison with those silver coupons that are “protected” by the selected scavengers.
- 1.5 To evaluate the outcome of the study project on its relevance and effectiveness in terms of its application to the preservation of silver objects which are on long term display at The Peranakan Museum.

## 2 First experiment

### 2.1 Setup

Each environment consisted of a control and 3 types of scavengers making a total of 4 setups. Each setup included a humidity strip; a strip of sterling silver (5 X 1 cm) that was barrier coated with Agateen lacquer on half a side to protect the surface from tarnishing while the other side exposed to  $H_2S$ ;  $H_2S$  in powder form as pollutant; fresh silica gel beads were incorporated to simulate a less than 55% RH micro-environment; and a  $H_2S$  scavenger (Figures 1 and 2). The 3 scavengers were Miracle Sac™, self-made zinc carbonate solution applied on acid-free blotter as described in Appendix A, and plain zinc carbonate ( $ZnCO_3$ ) powder. A relatively air-tight box (Nikon camera dry box) was used to construct a micro-environment across the 16 setups in order to achieve consistent and repeatable outcome. The full details of the setup were described in Table 2.1.

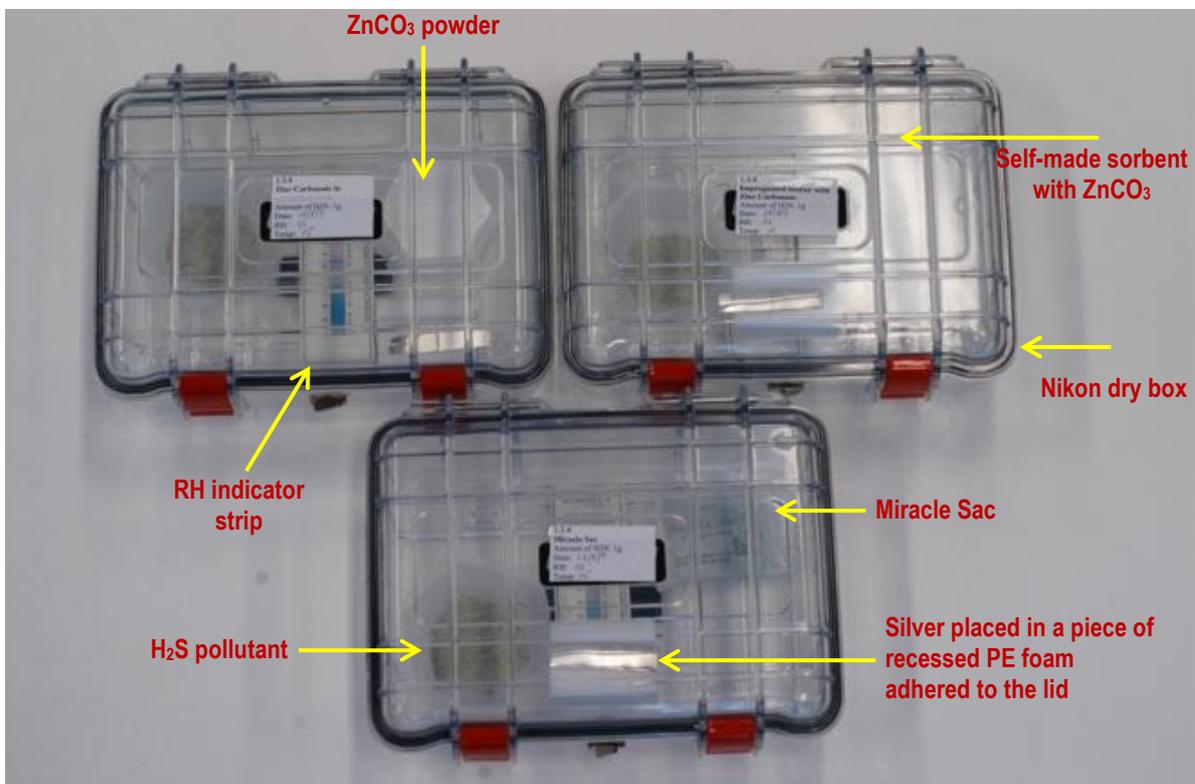


Figure 1: Setups for 55-65% RH museum environment (1.3.4)



Figure 2: Setup for Controls 1.4.2, 1.4.3 & 1.5

**Table 2.1: 16 setups for the evaluation of the 3 types of H<sub>2</sub>S scavengers in the first experiment**

No.	Setup & location	Scavenger	Relative humidity (RH)	Silica gel beads	Amt of H <sub>2</sub> S	Barrier coating on silver strip
1	1.3.1 Loading Bay	Miracle Sac™ (1 sachet 5g)*	Uncontrolled	-	1g	Half strip of silver coated with Agateen
2		Self-made sorbent with zinc carbonate (2g of ZnSO <sub>4</sub> soln to 2g of Na <sub>2</sub> CO <sub>3</sub> soln)*	Uncontrolled	-	1g	Half strip of silver coated with Agateen
3		Plain zinc carbonate powder (3.7g)*	Uncontrolled	-	1g	Half strip of silver coated with Agateen
4	1.5 Loading Bay, Control for 1.3.1	-	Uncontrolled	-	1g	Half strip of silver coated with Agateen
5	1.3.2 Conservation Workroom, Next to window	Miracle Sac™ (1 sachet)	Uncontrolled	-	0.5g	Half strip of silver coated with Agateen
6		Self-made sorbent with zinc carbonate (2g of ZnSO <sub>4</sub> soln to 2g of Na <sub>2</sub> CO <sub>3</sub> soln)	Uncontrolled	-	0.5g	Half strip of silver coated with Agateen
7		Plain zinc carbonate powder (3.7g)	Uncontrolled	-	0.5g	Half strip of silver coated with Agateen
8	1.4.3 Conservation Workroom, Control for 1.3.2	-	Uncontrolled	-	0.5g	Half strip of silver coated with Agateen
9	1.3.3 Objects Lab	Miracle Sac™ (1 sachet)	<55%	10 g	1g	Half strip of silver coated with Agateen
10		Self-made sorbent with zinc carbonate (2g of ZnSO <sub>4</sub> soln to 2g of Na <sub>2</sub> CO <sub>3</sub> soln)	<55%	10g	1g	Half strip of silver coated with Agateen

No.	Setup & location	Scavenger	Relative humidity (RH)	Silica gel beads	Amt of H <sub>2</sub> S	Barrier coating on silver strip
11		Plain zinc carbonate powder (3.7g)	<55%	10g	1g	Half strip of silver coated with Agateen
12	1.4.1 Objects Lab, Control for 1.3.3	-	<55%	10g	1g	Half strip of silver coated with Agateen
13	1.3.4 Objects Lab	Miracle Sac™ (1 sachet)	55-65%	-	1g	Half strip of silver coated with Agateen
14		Self-made sorbent with zinc carbonate (2g of ZnSO <sub>4</sub> soln to 2g of Na <sub>2</sub> CO <sub>3</sub> soln)	55-65%	-	1g	Half strip of silver coated with Agateen
15		Plain zinc carbonate powder (3.7g in dish)	55-65%	-	1g	Half strip of silver coated with Agateen
16	1.4.2 Objects Lab, Control for 1.3.4	-	55-65%	-	1g	Half strip of silver coated with Agateen

\* Refer to Appendix A

2.2 The following chosen locations to simulate the 4 environments mentioned in 1.3 were:

- 2.2.1 Location for 1.3.1 - Loading Bay (#1.5); this is a totally non-controlled open and sheltered environment. The temperature had an indicative range of 26-32°C and RH 52-91%;
- 2.2.2 Location for 1.3.2 - next to glass window in Conservation Workroom (#1.4.3); a non- controlled enclosed environment as it receives direct sunlight. An indicative single point reading for temperature near the window was 26°C;
- 2.2.3 Location for 1.3.3 - Objects Lab (1.4.1); to represent a museum/storage environment with RH lesser than 55%. Silica gel was used to enhance a drier environment for the setup. The temperature had an indicative range of 20-25°C and RH 54-71%;
- 2.2.4 Location for 1.3.4, Objects Lab (1.4.2); to represent a museum/storage environment with RH between 55 and 65%. No silica gel was used. The indicative temperature within the dry box without silica gel was 20-23.5°C and RH 57-64.5%.

### 2.3 Preparation of materials

The materials were handled and prepared in a consistent manner to avoid unintended or undesirable results from occurring during the experiment.

#### ***Silver as tarnish indicator***

Sterling silver consists of 92.5% silver and 7.5% copper. It was in a long strip of 5 cm width and was cut into 1 cm wide coupon. The silver was cleaned with ethanol and acetone separately using cotton wool. The cut edges were slightly curled as the strips were cut with a pair of scissors. Then approximately half the strip of the silver coupon was dipped into 1 part of Agateen lacquer #27 (nitro cellulose) premixed with 1 part of thinner for application on silver as a protective coating from being tarnished by  $H_2S$ . Once set, the silver coupon was laid elevated in the dry box. It was placed in and supported by a piece of recessed polyethylene (PE) foam and the foam was adhered to the lid on the inside of the dry box.

### ***Hydrogen sulphide $H_2S$ as pollutant***

$H_2S$  in powder form was used as the main source of pollutant to tarnish the silver coupon. In the first experiment, it was placed in the plastic dish. In the second experiment, it was placed in a glass petri dish covered over with a piece of finely woven nylon gauze.

### ***Silica gel incorporated in simulating a low RH environment (less than 55%)***

New silica gel beads with blue cobalt chloride indicator were used to lower the RH in the dry box and the beads would turn pink once saturated with moisture.

### ***Zinc carbonate ( $ZnCO_3$ ) powder as $H_2S$ scavenger***

The powder was used as it was. It was placed in a plastic dish.

### ***Miracle Sac™ as $H_2S$ scavenger***

Miracle Sac™ was a commercial product designed specifically to adsorb sulphur based pollutants. A sachet weighed 5g. It was composed of zinc oxide, copper oxide and aluminum oxide. It was marketed by Icel Developments Ltd at the time when the experiment was conducted.

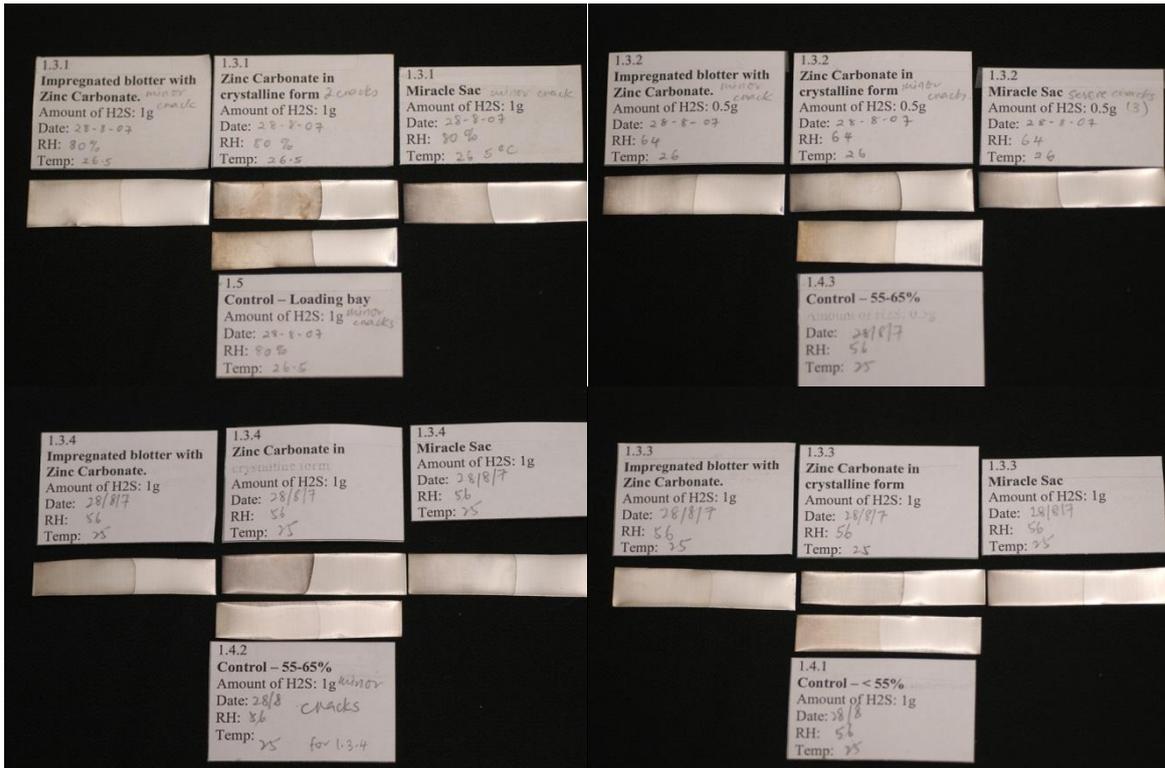
### ***Self-made $H_2S$ sorbent (acid-free blotter applied with zinc carbonate solution)***

Zinc carbonate  $ZnCO_3$  was obtained from mixing equal parts of zinc sulphate  $ZnSO_4$  (2g) solution to sodium carbonate  $Na_2CO_3$  (2g) solution. Then the solution of zinc carbonate  $ZnCO_3$  and sodium sulphate  $Na_2SO_4$  was smeared onto the surface of new acid-free blotter paper and air dried. Water was considered to be completely evaporated when the weight of the sorbent remained unchanged, carried out in a 55 – 65%RH environment. The final product had a flaky surface. Refer to Appendix A for more details.

## **3 Findings from the first experiment**

The tarnish on the silver coupons was compared across those in the same environment and against the control. The results were tabulated (Table 3.1) and coupons used in the same environment were photographed (Figures 3 – 6) together for ease of comparison.

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Figures 3 – 6: Visual assessment and comparison between silver coupons. From top left clockwise: open and uncontrolled environment (Loading Bay 1.3.1); enclosed and uncontrolled environment (Conservation Workroom 1.3.2); low RH environment (Objects Lab 1.3.3); and 55-65%RH environment (objects Lab 1.3.4)

Table 3.1: Key observations on silver coupons over a span of 3 months

Environment	Tarnish on control coupon	Tarnish on silver coupons from least to most based on the scavenger present			Other observations
<b>1.3.1</b> Loading Bay, uncontrolled, and open	<b>1.5</b> Black dots of corrosion, darker short edge of coupon, more tarnished than #SM and ^MS	<b>#SM</b> Black dots of corrosion, minimal black tarnish, ZnCO <sub>3</sub> on blotter does not appear flaky	<b>^MS</b> Black dots of corrosion, more tarnish on short edge	<b>*ZP</b> Black dots of corrosion, uneven tarnish	RH at loading bay was 80% and above while the reading in the dry boxes was 60 – 80%. Blotter adsorbed and desorbed moisture which might have influenced reaction between ZnCO <sub>3</sub> and H <sub>2</sub> S
<b>1.3.2</b> Conservation Workroom ( next to window with	<b>1.4.3</b> Uneven tarnish, some areas black, some areas	<b>SM</b> Black tarnish occurred quite rapidly, 1 black dot of corrosion,	<b>ZP</b> Uneven black tarnish. Short edge is darker, slight yellow	<b>MS</b> Black tarnish occurred quite rapidly. 1 black dot of corrosion,	RH inside dry boxes was 50 - 70%. All of them were exposed to direct sunlight.

Environment	Tarnish on control coupon	Tarnish on silver coupons from least to most based on the scavenger present			Other observations
direct sunlight), uncontrolled, and enclosed	yellow, darkened edges. Appeared least tarnished compared to those with scavengers	surface is quite evenly tarnished, edge is darker		dark edge, dull surface and even tarnish	Heat increased the rate of tarnishing.
<b>1.3.3</b> Objects Lab, <55%RH	<b>1.4.1</b> Some black dots, surface was slightly yellow, appeared least tarnished compared to those with scavengers, RH lower than the rest	<b>MS</b> Some black dots, slow tarnish, slight yellow	<b>SM</b> Some black dots, very slight and even tarnish	<b>ZP</b> 1 black dot, slight patchy tarnish	RH inside the box was 30 – 40%.
<b>1.3.4</b> Objects Lab, 55-65%	<b>1.4.2</b> Some black dots, only slight yellow, mainly 50-60%RH, Appeared least tarnished compared to those with scavengers	<b>MS</b> Some black dots, slow tarnishing, dark edges	<b>SM</b> Similar to MS	<b>ZP</b> More tarnished than SM and MS	RH inside the boxes was 50 – 70%.

<sup>#</sup>SM – Self-made H<sub>2</sub>S sorbent with zinc carbonate    <sup>\*</sup>ZP – plainly ZnCO<sub>3</sub> powder    <sup>^</sup>MS – Miracle Sac™

All the silver coupons were visually assessed with the loupe under daylight. It was obvious that the silver coupons in an open and uncontrolled environment tarnished the most, while in the low RH environment tarnished the least. The silver coupons in the 55-65%RH environment comparatively acquired more tarnish than the low RH environment and better than the coupons in the enclosed uncontrolled environment. The black dots of corrosion took place almost immediately on the silver coupons when the experiment started. This was likely caused by air movement and deposition of H<sub>2</sub>S powder onto the silver surface while the boxes were being handled. No further black dots of corrosion occurred subsequently. A few black dots also occurred on the area of the silver coupons coated with Agateen. This implied that the coating was slightly uneven and therefore unable to fully protect the silver. However, the coated surfaces remained shiny and no dulling. It appeared quite frequently that the edges of the silver coupons were

preferentially tarnished and darker. This was due to the surface structure of silver. Some coupons also had darker surface located at the short side of the uncoated silver because the coupon did not completely rest within the recessed PE foam but partially jutted out allowing it for more direct exposure to H<sub>2</sub>S.

It was observed that self-made sorbent with zinc carbonate performed the best in the uncontrolled environments. It was marginally better than Miracle Sac™ for the uncontrolled enclosed environment (1.3.2). It clearly appeared to be more effective in the uncontrolled open environment (1.3.1), which could be due to the moisture absorbing quality of the acid-free blotter with larger surface adsorption area, therefore slowing the rate of tarnishing. It was also observed that the ZnCO<sub>3</sub> on the acid-free blotter for 1.3.1 appeared cemented and much less flaky than the ones for 1.3.2, 1.3.3, and 1.3.4. On the other hand, Miracle Sac™ performed slightly better than self-made sorbent with zinc carbonate both in the low RH environment and 55-65%RH environment. The silver coupons with plain ZnCO<sub>3</sub> powder as scavenger appeared most tarnished compared with Miracle Sac™ and self-made sorbent with zinc carbonate.

The lower amount of pollutant H<sub>2</sub>S (0.5g) for 1.3.2 (uncontrolled enclosed environment) had no obvious visible influence on the level of tarnish when compared to other environments with higher quantity of H<sub>2</sub>S. The control coupon was not very much better than the control coupon of 1.3.1 (uncontrolled open environment) and definitely much worse than the control coupons of 1.3.3 and 1.3.4. The slight elevation in temperature would have contributed to the tarnishing of the silver coupons.

Theoretically, all control coupons should be more tarnished than the adjacent silver coupons with scavengers in the same environment. But this only occurred to the uncontrolled open environment (1.3.1). The rest of the control coupons (for 1.3.2, 1.3.3, and 1.3.4) were least tarnished compared to all the coupons with scavengers in the same environments. This could be due to the layout of the scavengers and H<sub>2</sub>S in relation to the air flow within the dry boxes. Based on the 4 control coupons, the coupons for low RH environment and 55-65%RH environment tarnished the least and the coupon for uncontrolled open environment (1.3.1) tarnished the most. This implied that moisture, and higher temperature contributed significantly to tarnishing. The lesser moisture there is, and lower the temperature, the slower the rate of tarnishing.

Last but not least, coating silver with Agateen has evidently shown that it was effective in protecting silver from tarnishing whether in controlled or uncontrolled environment, as the coated side of the silver coupons did not tarnish at all, except a few black spots of corrosion caused by the deposition of H<sub>2</sub>S particles onto the surface.

#### **4 Second experiment**

In the second experiment, the same air-tight box (Nikon camera dry box) was used across the 16 setups. The setup was similar to the first experiment and the materials were also prepared the same way. Each setup included a humidity indicator strip; a strip of sterling silver that was barrier coated with Agateen on half a side to protect the surface from tarnishing while the other side exposed to H<sub>2</sub>S; H<sub>2</sub>S in powder form as pollutant; fresh silica gel for simulating a less than 55% RH micro-environment; and a H<sub>2</sub>S scavenger.

#### 4.1 Changes made to the setup

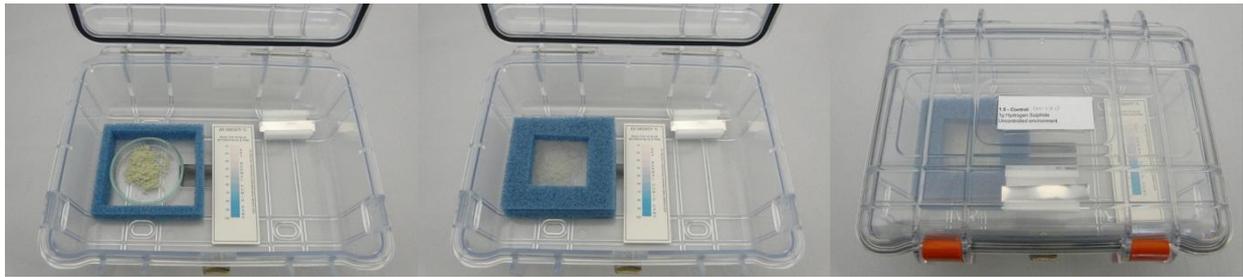
Based on the findings from the previous experiment, zinc carbonate ( $ZnCO_3$ ) powder was removed from the second experiment. The 3 types of scavengers that would be tested were Miracle Sac™, self-made sorbent with zinc carbonate applied on acid-free blotter as described in Appendix A, and Seachem's MatrixCarbon™ spherical beads. MatrixCarbon™ is activated spherical carbon. It is designed to filter organic matter in water. The difference between MatrixCarbon™ and activated carbon used for air filtration is the size of its pores which allow water to pass through the carbon. For the purpose of monitoring, 5g of MatrixCarbon™ beads were wrapped and stitched up in a woven nylon gauze fabric with cotton thread to avoid the beads from rolling about. The duration of the experiment spanned over 16 months. The full details of the setup were described in Table 4.1.

**Table 4.1: 16 setups for the evaluation of the 3 types of H<sub>2</sub>S scavengers in the second experiment**

No.	Setup & location	Scavenger	RH	Silica gel beads	Amt of H <sub>2</sub> S	Barrier coating on silver strip
1	1.3.1 Loading Bay	Miracle Sac™ (1 sachet)	Uncontrolled	-	1g	Half strip of silver coated with Agateen
2		Self-made sorbent with zinc carbonate (2g of ZnSO <sub>4</sub> soln to 2g of Na <sub>2</sub> CO <sub>3</sub> soln)	Uncontrolled	-	1g	Half strip of silver coated with Agateen
3		MatrixCarbon™ (5g)	Uncontrolled	-	1g	Half strip of silver coated with Agateen
4	1.5 Loading Bay, Control for 1.3.1	-	Uncontrolled	-	1g	Half strip of silver coated with Agateen
5	1.3.2 Objects Office	Miracle Sac™ (1 sachet)	Uncontrolled	-	0.5g	Half strip of silver coated with Agateen
6		Self-made sorbent with zinc carbonate (2g of ZnSO <sub>4</sub> soln to 2g of Na <sub>2</sub> CO <sub>3</sub> soln)	Uncontrolled	-	0.5g	Half strip of silver coated with Agateen
7		MatrixCarbon (5g)	Uncontrolled	-	0.5g	Half strip of silver coated with Agateen
8	1.4.3 Objects Office, Control for 1.3.2	-	Uncontrolled	-	0.5g	Half strip of silver coated with Agateen
9	1.3.3 Objects Lab	Miracle Sac™ (1 sachet)	<55%	10 g	1g	Half strip of silver coated with Agateen
10		Self-made sorbent	<55%	10g	1g	Half strip of silver

No.	Setup & location	Scavenger	RH	Silica gel beads	Amt of H <sub>2</sub> S	Barrier coating on silver strip
		with zinc carbonate (2g of ZnSO <sub>4</sub> soln to 2g of Na <sub>2</sub> CO <sub>3</sub> soln)				coated with Agateen
11		MatrixCarbon™ (5g)	<55%	10g	1g	Half strip of silver coated with Agateen
12	1.4.1 Objects Lab, Control for 1.3.3	-	<55%	10g	1g	Half strip of silver coated with Agateen
13	1.3.4 Objects Lab	Miracle Sac™ (1 sachet)	55-65%	-	1g	Half strip of silver coated with Agateen
14		Self-made sorbent with zinc carbonate (2g of ZnSO <sub>4</sub> soln to 2g of Na <sub>2</sub> CO <sub>3</sub> soln)	55-65%	-	1g	Half strip of silver coated with Agateen
15		MatrixCarbon™ (5g)	55-65%	-	1g	Half strip of silver coated with Agateen
16	1.4.2 Objects Lab, Control for 1.3.4	-	55-65%	-	1g	Half strip of silver coated with Agateen

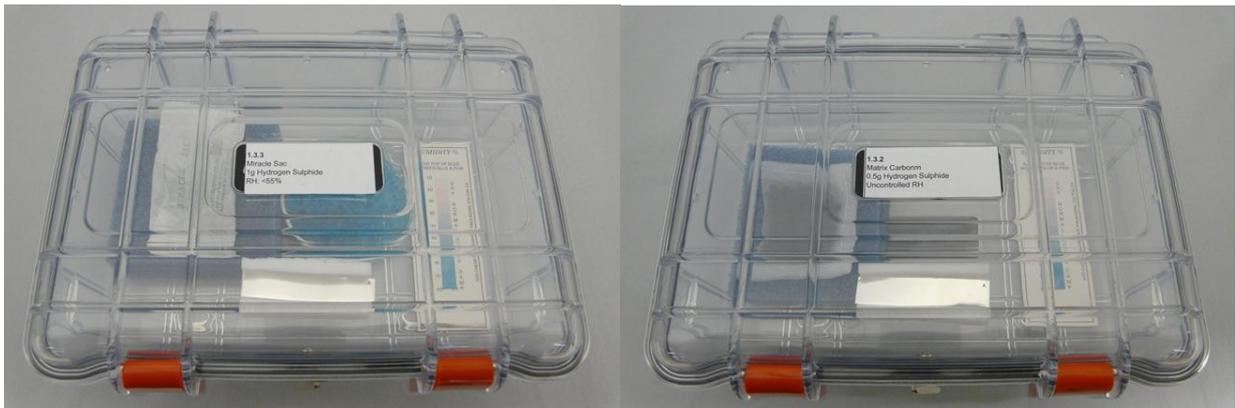
In the second experiment, some changes were made to the setup. The H<sub>2</sub>S used in the control setups was covered over with a piece of fine woven nylon gauze (Figures 7 – 9) in order to reduce movement of the powder through handling. For the other setups, scavengers were placed directly on top of the H<sub>2</sub>S pollutant to improve filtration (Figures 10 – 14). The silver coupon continued to be elevated in the dry box. It was placed in a piece of recessed PE foam and the foam was in turn adhered to the lid on the inside of the dry box. Another change made to the experiment was the change of monitoring location for enclosed and uncontrolled environment (1.3.2). In the first experiment, the space next to the window in Conservation Workroom was chosen. In the second experiment, the office space was selected as it better represented an enclosed air-conditioned yet non-RH controlled space without direct exposure to sunlight. The temperature had an indicative range of 22.5-25°C and RH 50-64%.



Figures 7 – 9: Layout of control setup. H<sub>2</sub>S powder is covered over with a piece of fine woven nylon gauze. Silver coupon is placed in a piece of recessed PE foam adhered to the lid on the inside of the dry box



Figures 10 - 12: Layout of self-made H<sub>2</sub>S sorbent with zinc carbonate. The scavenger is placed directly on top of the pollutant H<sub>2</sub>S



Figures 13 – 14: Layouts of Miracle Sac™ and MatrixCarbon™

## 5 Findings from the second experiment

The tarnish on the silver coupons was compared across those in the same environment against its control. The results were tabulated (Table 5.1) and photographed (Figures 15 – 18) together for ease of comparison. The method of assessment was the same as the first experiment. In addition, a clean and unused silver coupon that was barrier coated with Agateen on half a side was used as a visual reference to gauge the level of tarnish on all the 16 coupons including the controls.

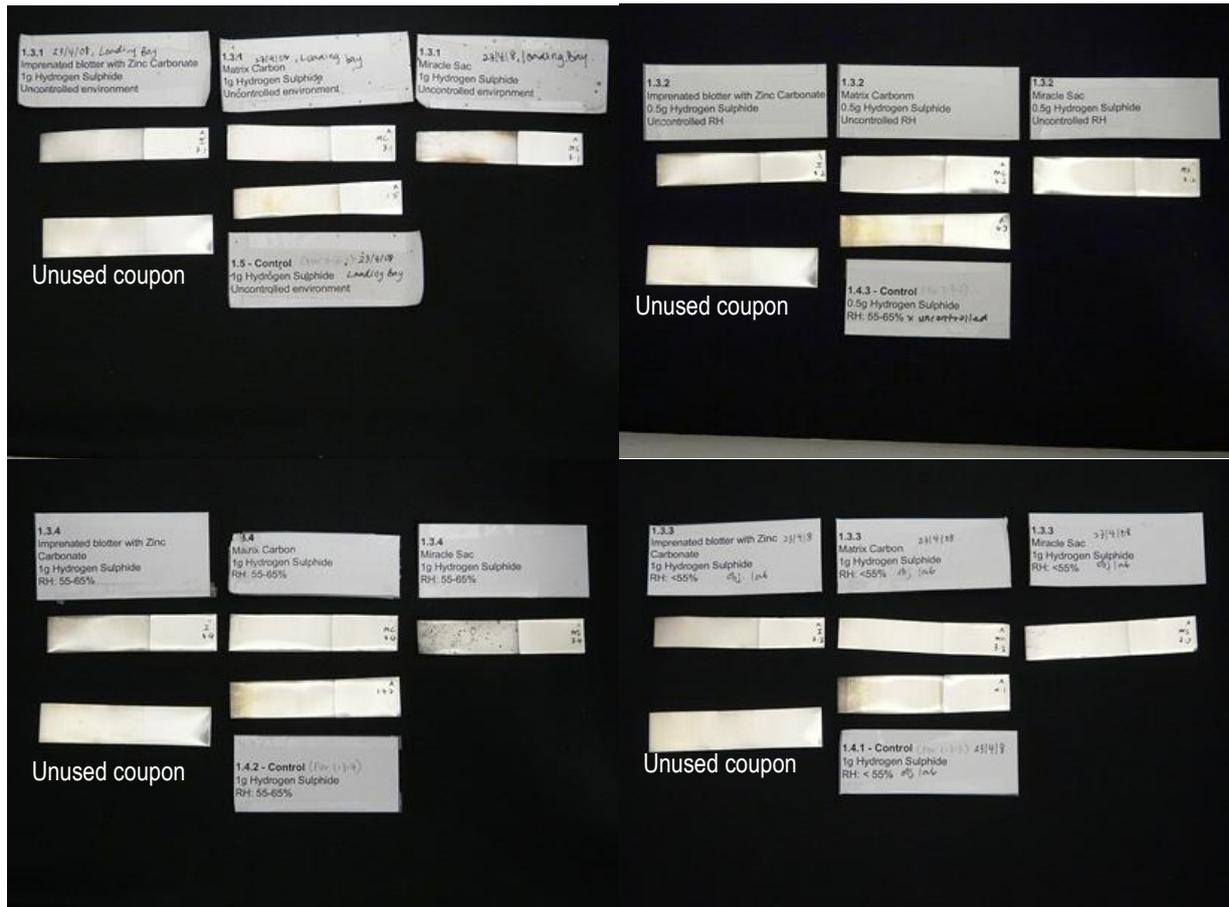
Table 5.1: Key observations on silver coupons over a span of 16 months

Environment	Tarnish on control coupon	Tarnish on silver coupons from least to most based on the scavenger present			Other observations
1.3.1 Loading Bay, uncontrolled, and open	1.5 Only slightly more tarnished	*MC Slight tarnish, darker edges	#SM 1 black dot of corrosion, evenly	^MS Whole surface tarnish,	RH inside dry boxes was mainly 60 – 80%

Environment	Tarnish on control coupon	Tarnish on silver coupons from least to most based on the scavenger present			Other observations
	than *MC.		tarnished surface, darker edges	darker edges, Silver coupon fell onto the RH indicator strip, causing the contact areas more corroded	
<b>1.3.2</b> Objects Office, uncontrolled, and enclosed	<b>1.4.3</b> 3 black dots of corrosion, unevenly yellowed with patches of black, most tarnished compared to those with scavengers	<b>MC</b> Slight tarnish, darker edges	<b>MS</b> Evenly tarnished surface, slightly darker edges than MC	<b>SM</b> Very black edges compared to the other 2	RH inside dry boxes was mainly 40 – 60%
<b>1.3.3</b> Objects Lab < 55%RH	<b>1.4.1</b> Silica gel turned pink in a week, short edge was very much darker, most tarnished compared to those with scavengers	<b>MC</b> Silica gel turned pink within days, surface slightly dull and edge slightly yellow	<b>MS</b> Silica gel turned pink in a week, 1 black dot, darker edges	<b>SM</b> Silica gel turned pink within days and humidity strip showed higher RH, even tarnish and darker edges	RH inside dry boxes was mainly 20 – 60%
<b>1.3.4</b> Objects Lab 55 - 65%	<b>1.4.2</b> A black dot, darker short edge, more tarnished than MC	<b>MC</b> 1 black dot, slight tarnish but darker edges	<b>SM</b> 1 black dot, surface was more black than MC and edges were visibly darker	<b>MS</b> Box toppled during ceiling collapse in the lab, and coupon was stained with H <sub>2</sub> S resulting many black spots, surface very tarnished	RH inside dry boxes was mainly 40 – 60%

<sup>#</sup>SM – Self-made sorbent with zinc carbonate    <sup>\*</sup>MC – MatrixCarbon™    <sup>^</sup>MS – Miracle Sac™

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Figures 15 – 18: Visual assessment and comparison between silver coupons. From top left clockwise: open and uncontrolled environment (Loading Bay 1.3.1); enclosed and uncontrolled environment (Objects Office 1.3.2); low RH environment (Objects Lab 1.3.3); and 55-65%RH environment (objects Lab 1.3.4)

All the silver coupons were visually assessed with the loupe under daylight. With the scavenger now placed directly above the pollutant, the level of tarnish was less on the coupons when compared in adjacent with those in the same environment from the previous experiment except Low RH environment (1.3.3). The number of black dots of corrosion was also substantially reduced after a change in the layout. Unfortunately, the coupons monitoring Miracle Sac for 1.3.1 and 1.3.4 could not provide good indication on its performance. High RH of the uncontrolled open environment did not seem to impact significantly on level of tarnish generally. The level of tarnish under the low RH environment was moderately less than those in the other 3 environments. The edges of the silver coupons have preferentially tarnished and darker and this was due to the surface structure of silver. Some coupons also have darker surface located at the short side of the uncoated silver because the coupon jugged out from the recessed PE foam leading to more direct exposure to H<sub>2</sub>S.

MatrixCarbon™ clearly performed the best in all the environments compared with the other 2 scavengers and also less tarnished than the respective control coupons. Self-made H<sub>2</sub>S sorbent with zinc carbonate appeared more effective than Miracle Sac™ under uncontrolled and open environment (1.3.1) which could be due to the moisture absorbing quality of the acid-free blotter and larger surface adsorption area for H<sub>2</sub>S, therefore slowing the rate of tarnishing. On the other hand, Miracle Sac™ seemed more

effective than self-made sorbent with zinc carbonate for both low RH environment (1.3.3) and uncontrolled and enclosed environment (1.3.2).

Control coupons were expected to be most tarnished in the absence of scavengers for all environments, but not for 1.3.1 and 1.3.4. The most possible explanation could be that the fine woven nylon gauze had effectively acted as a barrier in preventing the H<sub>2</sub>S powder from dispersing via air movement resulted from air exchange between inside and outside of the dry box.

Comparing all 4 control coupons together, it turned out that the coupon for uncontrolled and open environment was the least tarnished while the coupon for low RH environment tarnished the most. Based on the summary of the observations mentioned above, the silica gel exhausted quickly in a week. Cracks were also observed on some of the Nikon dry boxes over time. This led to higher number of air exchanges and directly influenced the RH within the box and therefore impacted on tarnishing of silver.

## **7. Conclusion of the study project**

All evaluations were based on visual assessment. Out of the 4 types of scavengers, MatrixCarbon™ is most effective in reducing tarnishing on silver in comparison with self-made H<sub>2</sub>S sorbent with zinc carbonate and commercial preservation product Miracle Sac™, according to the stated setups. Furthermore, the silver coupons with MatrixCarbon™ are evidently less tarnished than the control coupons across all the 4 environments. Hence it would be suitable for use in reasonably small enclosed and air-tight spaces even without RH control capability. Generally, in order for scavenging to work properly and effectively, factors such as air-flow, air-tightness of a given enclosure, quantity and placement of scavengers in relation to where air exchanges take place, suitability in its application to a particular situation, etc are important considerations.

By and large, the performance of the tested scavengers conducted through this study project must not be taken as conclusive. Molar mass was primarily applied as a standard of measure in order to allow the hypothetical evaluation comparable. In general, all sorbent materials require regular replacement and are not self-indicating when they are exhausted. Furthermore, the use of scavengers is not straight forward as there are many situational factors governing its suitability in terms of its application.

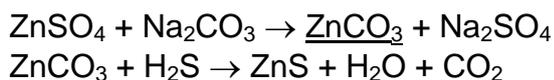
In view of the application of scavengers in The Peranakan Museum, review on condition of the silver objects in relation to its current display technique should be made to ascertain a feasible preservation strategy in totality.

## Appendix A

The scavengers selected for evaluation do not just adsorb hydrogen sulphide, but also moisture and traces of other sulphur compounds such as carbonyl sulphides and pollutants present in the atmosphere. Due to the difference in the adsorption qualities, the quantity of zinc carbonate ( $\text{ZnCO}_3$ ) powder, self-made hydrogen sulphide ( $\text{H}_2\text{S}$ ) sorbent with  $\text{ZnCO}_3$  and  $\text{H}_2\text{S}$  powder were calculated using the chemical formula equation (A.1). Hence 3.7g of  $\text{ZnCO}_3$  theoretically reacts to 1g of  $\text{H}_2\text{S}$  (A.2). It was stated on the website (<http://www.cwaller.de/sorbents.htm>, accessed 28 August 2006) that 1 sachet of Miracle Sac™ (5g) could absorb more than 1g of  $\text{H}_2\text{S}$  (A.3). Since there wasn't specification provided what quantity of MatrixCarbon™ (A.4) was required to specifically adsorb  $\text{H}_2\text{S}$ , a parallel quantity of 5g was used in the experiment to attain comparable results.

### A.1) Quantity of self-made $\text{H}_2\text{S}$ sorbent with zinc carbonate ( $\text{ZnCO}_3$ ) required per setup

Self-made  $\text{ZnCO}_3$  solution was prepared by mixing 2g of  $\text{ZnSO}_4$  in de-ionised water to 2g of  $\text{Na}_2\text{CO}_3$  in de-ionised water. This final solution was then applied to new acid-free blotter. Once water has fully evaporated, the sorbent could be used in the experiment.



Mathematical calculation for 1 mole of  $\text{ZnCO}_3$  and 1 mole of  $\text{H}_2\text{S}$   
1 mole of  $\text{ZnCO}_3 \approx 125\text{g}$   
1 mole of  $\text{H}_2\text{S} \approx 34\text{g}$

Hence, about 3.7g of  $\text{ZnCO}_3$  would be required to react with 1g of  $\text{H}_2\text{S}$ .

### A.2) Quantity of plain zinc carbonate ( $\text{ZnCO}_3$ ) powder required per setup

As calculated in (A.1) above, about 3.7g of  $\text{ZnCO}_3$  would be required to react with 1g of  $\text{H}_2\text{S}$ .

### A.3) Quantity of Miracle Sac™ required per setup

(<http://www.cwaller.de/sorbents.htm>, information on Miracle Sac™ was removed since last access on 26 Sep 2012)

Based on specification provided by manufacturer in 2006, 1 sachet weighed 5g and absorbed more than 1g  $\text{H}_2\text{S}$ . The stated website was recently accessed on 26 Sep 2012, and information on Miracle Sac™ could not be found.

### A.4) Quantity of MatrixCarbon™ spherical beads required per setup

The specification provided is for use in water. Therefore 5g of MatrixCarbon™ was used in the experiment to match the quantity of 1 sachet of Miracle Sac™.

## Materials List

<b>Brand</b>	<b>Supplier</b>
<b>Miracle Sac™</b> 1 bag weighs 5g, adsorbs > 1g H <sub>2</sub> S 35 sachets for 1m <sup>3</sup> space for 100 exchanges per day	Icel Developments Ltd, UK <a href="mailto:CWaller@t-online.de">CWaller@t-online.de</a> 15 Fairview way Edgware Middlesex HA8-8JE
<b>Hydrogen sulphide (H<sub>2</sub>S) in powder form</b>	Kanto Chemical Co., Inc Kanto Kagaku Singapore Pte Ltd 72, Tuas Ave 11 S639092
<b>Silica gel with blue cobalt choride indicator</b>	Photo prints processing shop
<b>Nikon camera dry box</b>	Alan Photo Trading Blk 1 Rochor Canal Road #01-38 Sim Lim Square
<b>Humidity strips</b>	Conservation material supplies store
<b>Acid-free blotter</b>	Conservation material supplies store
<b>Zinc carbonate, basic (ZnCO<sub>3</sub>)</b>	Kanto Chemical Co., Inc Kanto Kagaku Singapore Pte Ltd 72, Tuas Ave 11 S639092
<b>Zinc sulphate, anhydrous (ZnSO<sub>4</sub>)</b>	Kanto Chemical Co., Inc Kanto Kagaku Singapore Pte Ltd 72, Tuas Ave 11 S639092
<b>Sodium carbonate, decahydrate (Na<sub>2</sub>CO<sub>3</sub>.10H<sub>2</sub>O)</b>	Kanto Chemical Co., Inc Kanto Kagaku Singapore Pte Ltd 72, Tuas Ave 11 S639092
<b>Agateen lacquer #27, and Agateen thinner #1</b>	Talas, online conservation supplies store
<b>925 Sterling Silver</b>	Yuen Kee Ho Unit C4 G/F, Phase 2 Hang Fung Industrial building, 2G Hok Yuen Street, Hunghom, Kowloon
<b>MatrixCarbon™ spherical beads</b>	Aqua Star Trading Blk 934 Yishun Central 1, #01-51/53/55 S760934

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