



SiliaMetS®

## SiliaMetS Thiol and DMT Stability in Aqueous Media

SiliaMetS Metal Scavengers were developed to eliminate post-reaction purification issues with metallic residues. While generally used in organic solvents, due to recent environmental laws and concerns, green chemistry in aqueous media has gained popularity. Metal Scavengers have been shown to be effective in aqueous environments, a key opportunity for greening chemical processes. This Application Note demonstrates the chemical stability of SiliaMetS DMT and SiliaMetS Thiol in water.

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about SiliaMetS in our brochure “Solutions for Scavenging of Metal & Organic Impurities”.



To make chemistry greener, many processes are swapping organic solvents for aqueous environments. Most SiliaMetS Metal Scavengers are compatible with aqueous as well as organic solvents (*Table 1*). The following experiments were conducted by the R&D team to demonstrate the chemical stability of two popular SiliaMetS (*DMT and Thiol*) in aqueous conditions over a fixed period of time and temperature.

**Table 1:** Scavengers' compatibility in organic and aqueous solvents chart

Scavengers' compatibility in organic and aqueous solvents chart														
Solvent Type	Amine	Diamine	Triamine	Toxic acid	DEAM	AMPA	Cysteine	DMT	DOTA	Imidazole	TAAcOH	TAAcONa	Thiol	Thiourea
Organic	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Aqueous	✗	✗	✗	✓	✓	✓	✗	✓	✓	✓	✓	✓	✓	✓

	Compatible
	Not compatible

The two SiliaMetS were added to deionized water, one test was held at room temperature (*r.t.*) and the other at 60°C. The vials were shaken manually once a day and samples were taken over the course of a week. Chemical stability and absence of leaching was tested by CNS analysis. In addition, pH consistency was recorded, and scavenging performance was assessed at each time point.

## Leaching and Degradation Study

CNS analysis allows to determine if the material has leached or deteriorated. In such cases, this would result in a loss in terms of carbon (C %), nitrogen (N %) and sulfur (S %) load and would then be observed by this analysis. Prior to this assessment, the samples were exposed to an aqueous environment from 10 minutes to 7 days, at *r.t.* and 60°C, before being filtered and dried. Carbon and sulfur loading content were recorded for Thiol (*Table 2*), and carbon, nitrogen and sulfur loading content were recorded for DMT (*Table 3*).

**Table 2:** Degradation and leaching study of SiliaMetS Thiol with an initial carbon loading of 6.6 % and sulfur loading of 4.7 %

Degradation and leaching study of SiliaMetS Thiol with an initial carbon loading of 6.6 % and sulfur loading of 4.7 %				
Time point	r.t.		60°C	
	C %	S %	C %	S %
Start	6.6	4.7	N/A	N/A
10 minutes			N/A	N/A
60 minutes				
4 hours				
24 hours				
7 days				

	No significant change (from 0 to < 1 % difference)
	Light loss (from 1.0 to < 2.0 % difference)
	Fair loss (from 2.0 – 3.0 % difference)
	Substantial Loss (> 3.0 % difference)

The data demonstrates that Thiol did not experience any degradation or leaching over the course of the seven days in an aqueous environment even at 60°C; since the sulfur content remained constant, and the minimal carbon loss (*less than 0.7 %*) was most likely due to loss of residual solvent or uncertainty. The same experiment was performed with SiliaMetS DMT.

**Table 3:** Degradation and leaching study of SiliaMetS DMT with initial carbon loading of 9.7 %, nitrogen loading of 4.5 % and sulfur loading of 3.5 %

Degradation and leaching study of SiliaMetS DMT with initial carbon loading of 9.7 %, nitrogen loading of 4.5 % and sulfur loading of 3.5 %						
Time point	r.t.			60°C		
	C %	S %	N %	C %	S %	N %
Start	9.7	4.5	3.5	N/A	N/A	N/A
10 minutes				N/A	N/A	N/A
60 minutes						
4 hours						
24 hours						
7 days						

	No significant change (from 0 to < 1 % difference)
	Light loss (from 1.0 to < 2.0 % difference)
	Fair loss (from 2.0 – 3.0 % difference)
	Substantial Loss (> 3.0 % difference)

Data in Table 3 shows that SiliaMetS DMT did not degrade nor leach when exposed to aqueous conditions up to seven days, even while heating to 60°C. The loss of carbon observed could be due to the residual solvent in the silica since both nitrogen and sulfur content remained stable over time.

Overall, no degradation of the Scavengers' structures was observed over the time studied.

## pH Study

To further confirm the chemical stability of the Scavengers in aqueous conditions, the pH of the solutions was recorded at r.t. and 60°C at the same time points over the course of the experiment after the Scavenger was filtered out (Table 4).

**Table 4:** pH of aqueous solution of SiliaMetS Thiol and DMT at r.t. and 60°C

pH of aqueous solution of SiliaMetS Thiol and DMT at r.t. and 60°C				
Time point	Thiol		DMT	
	r.t.	60°C	r.t.	60°C
Start	9.9	N/A	8.4	N/A
10 minutes				N/A
60 minutes				
4 hours				
24 hours				
7 days				

	No significant change (from 0 to < 1 % difference)
	Light loss (from 1.0 to < 2.0 % difference)
	Fair loss (from 2.0 – 3.0 % difference)
	Substantial Loss (> 3.0 % difference)

Over a period of up to 7 days in an aqueous solution the pH was stable for both SiliaMetS Thiol and DMT at room temperature and 60°C. In other words, the Scavengers did not affect the solution's pH over the time of the experiment, which suggests that no degradation observable by a change in pH occurred on the Scavengers over that same period.



## Scavenging Performance Study

The first sets of data evaluated stability; however, it is also important that Scavengers perform and not lose scavenging efficiency. Samples taken at each time point were filtered and dried before being mixed with a palladium (*Pd*) catalyst (4 molar equivalents of the Scavenger) in water. Scavenging yield was measured by residual Pd content as shown by ICP-OES. Results are given in Table 5 (*Thiol*) and Table 6 (*DMT*).

The catalyst used to test Scavenger performance was palladium acetate ( $Pd(OAc)_2$ ) for SiliaMetS Thiol. For SiliaMetS DMT, it was previously shown that scavenging of tetrakis triphenylphosphine ( $Pd(PPh_3)_4$ ) was more capricious, hence it was chosen here as the palladium source to rigorously check the performance of the Scavenger.

**Table 5:**  $Pd(OAc)_2$  Scavenging yield with SiliaMetS Thiol exposed to water

 <b><math>Pd(OAc)_2</math> Scavenging yield with SiliaMetS Thiol exposed to water</b>		
Time point	r.t. (%) 1 h	60°C (%) 1 h
Start	92	N/A
10 minutes	95	N/A
60 minutes	95	93
4 hours	96	93
24 hours	97	93
7 days	97	97

It can be noted that the reactivity of the SiliaMetS Thiol was not negatively affected by the exposure to water at r.t. or at 60°C and the scavenging yields remained over 90 % for all tested samples.

Moving along, the scavenging yield was tested with SiliaMetS DMT. Scavenging efficiency was this time measured after one and two hours.

**Table 6:**  $Pd(PPh_3)_4$  Scavenging yield with SiliaMetS DMT exposed to water

 <b><math>Pd(PPh_3)_4</math> Scavenging yield with SiliaMetS DMT exposed to water</b>				
Time point	r.t. (%)		60°C (%)	
	1 h	2 h	1 h	2 h
Start	97	99	N/A	N/A
10 minutes	95	98	N/A	N/A
60 minutes	95	99	95	95
4 hours	96	99	99	100
24 hours	97	99	99	100
7 days	97	100	100	100

Not only did water exposure not affect the scavenging yield of SiliaMetS DMT on palladium tetrakis triphenylphosphine, but yields up to 100 % were also obtained after 2 hours of scavenging showing just how efficient the Scavenger still was.

Hence, no loss of performance was observed for either Scavenger after being exposed to room temperature water and warm water over a period of up to seven days.



## Conclusion

In conclusion, SiliaMetS Thiol and SiliaMetS DMT were exposed to an aqueous environment at room temperature and 60°C for up to seven days without being adversely impacted. With the move towards friendlier chemical processes for the environment, the use of aqueous solvents will become increasingly popular. Metal Scavengers being an important part of post-reaction purifications, it was imperative to evaluate their stability and efficiency with these solvents. The purpose of this experiment was to justify using aqueous (*and greener*) solvents in purifications using Metal Scavengers without loss of efficiency.

Based on CNS analysis, pH measurements and scavenging experiments, both SiliaMetS Thiol and DMT showed no degradation and maintained their scavenging performance over the time studied.

Other Scavengers found in the portfolio, although not included in this Application Note, are also compatible in aqueous environments (*Table 1*).

While the Scavengers' compatibilities with aqueous solvents are demonstrated, limits to swapping solvents can arise from the compound of interest's solubility in these solvents. When the compounds are soluble in any solvent, SiliaMetS are a straightforward solution to green processes with the possibility of working in several green solvents, including water for some.

When it comes to the green transition, Scavengers are here to help and there is sure to be a SiliaMetS right for the application.

