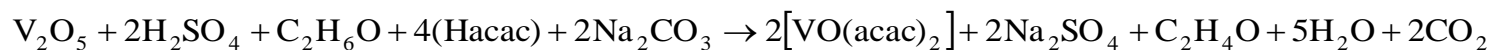


Synthesis of vanadyl acetylacetonate – Protocol D



Reaction. Boil for 30 minutes a mixture containing 5.0 g (27 mmol) vanadium pentoxide, 13 mL water, 9 mL (166 mmol) concentrated sulphuric acid (about 207% excess) and 25 mL (428 mmol) ethanol (about 1458% excess). Filter the mixture and treat the cold filtrate with 13 mL (126 mmol) of acetylacetone (about 14% excess). Add an aqueous sodium carbonate solution (14% by weight) in small increments with vigorous stirring, measuring the pH after each addition.

Isolation. Filter off the resulting solid, wash with cold water until negative test with barium and dry in a desiccator over phosphorus pentoxide.

Purification. Not prescribed.

Safety. See hazards associated with the reagents in Table 1.

Greenness Assessment. The evaluation was performed using the Green Star (GS) and the results are shown in Figure 1.

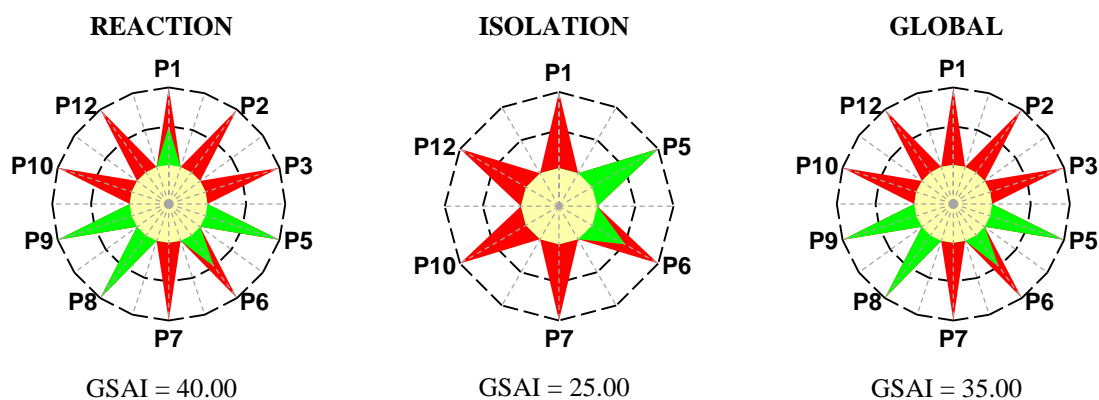


Figure 1. Greenness assessment (GS) for the synthesis of vanadyl acetylacetonate

Construction of the GS

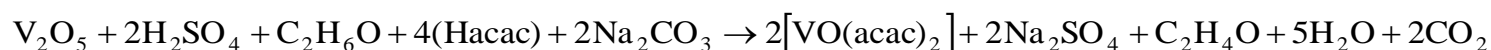


Table 1 presents the hazards and scores associated with the substances involved and Table 2 presents the scores used to construct the green stars.

Table 1. Hazards for the synthesis of vanadyl acetylacetonate, protocol D^a

Substances involved	Step			Hazard code	Score: hazards to...		
	R	I	Pu		HH	E	P
Stoichiometric reagents							
Acetylacetone ^c (CAS 123-54-6)	✓			H226, H302	2	1	2
Ethanol ^b (CAS 64-17-5)	✓			H225	1	1	3
Sodium carbonate (CAS 497-19-8)	✓			H319	2	1	1
Sulphuric acid (CAS 7664-93-9)	✓			H314	3	1	1
Vanadium pentoxide (CAS 1314-62-1)	✓			H302, H332, H335, H341, H361, H372, H411	3	3	1
Auxiliary substances							
Solvents							
Water ^{a,b}	✓	✓		-	1	1	1
Product							
Vanadyl acetylacetonate (3153-26-2)	✓	✓		H302, H315, H319, H335	2	1	1
Waste							
Acetylacetone ^c (excess)		✓		H226, H302	2	1	2
Carbon dioxide	✓			H280	1	1	2
Ethanal		✓		H224, H302, H317, H319, H335, H351	3	1	3
Ethanol ^b		✓		H225	1	1	3
Sodium carbonate (aqueous solution)		✓		-	1	1	1
Sodium sulphate (aqueous solution)		✓		-	1	1	1
Sulphuric acid (dilute solution)		✓		-	1	1	1
Vanadyl sulphate hydrate	✓			H302	2	1	2
Water ^{a,b}		✓		-	1	1	1

^a R – Reaction; I – Isolation; Pu – Purification; HH – Human Health; E – Environment; P – Physical

^a Renewable; ^b Degradable to innocuous products; ^c Degradable

Table 2. Scores used to construct the green star for the synthesis of vanadyl acetylacetonate, protocol D^a

Green Chemistry Principle	Reaction		Isolation		Global	
	s	Explanation	s	Explanation	s	Explanation
P1 Prevention	2	Vanadyl sulphate hydrate, H302	1	Ethanal, H351	1	Ethanal, H351
P2 Atom Economy	1	Excess of reagents > 10%, formation of by-products		NA	1	Excess of reagents > 10%, formation of by-products
P3 Less hazardous chemical synthesis	1	Vanadium pentoxide, H341, H361, H372, H411, sulphuric acid, H314, ethanal, H351		NA	1	Vanadium pentoxide, H341, H361, H372, H411, sulphuric acid, H314, ethanal, H351
P5 Safer solvents and auxiliary substances	3	Water	3	Water	3	Water
P6 Increase energy efficiency	2	0 °C ≤ T ≤ 100 °C	2	0 °C ≤ T ≤ 100 °C	2	0 °C ≤ T ≤ 100 °C
P7 Use renewable feedstocks	1	Substances not renewable	1	Substances not renewable	1	Substances not renewable
P8 Reduce derivatives	3	One stage		NA	3	One stage
P9 Catalysts	3	Without catalysts		NA	3	Without catalysts
P10 Design for degradation	1	Substances not degradable	1	Substances not degradable	1	Substances not degradable
P12 Safer chemistry for accident prevention	1	Vanadium pentoxide, H341, H361, H372, sulphuric acid, H314, ethanal, H224, ethanol, H225	1	Ethanal, H224	1	Vanadium pentoxide, H341, H361, H372, sulphuric acid, H314, ethanal, H224, ethanol, H225

^as – Score; NA – Not applicable

References

Osorio, V.K.L.; Ferreira, M. The Synthesis of Oxobis(2,4-pentanedioato)vanadium(IV) Revisited. *Química Nova*. **1991**, *14*(3), 162-164.