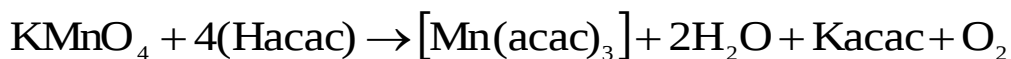


Synthesis of manganese(III) acetylacetonate – Protocol H



Reaction. Dissolve 5.0 g (31.7 mmol) of powdered potassium permanganate in the minimum volume of water by slight warming over a steam bath and then filter the solution. Add 22.0 g (220 mmol) of acetylacetone (about 73.5% excess) with vigorous stirring. Stir the mixture for 5 minute over a steam bath and then allow to cool for 10 minutes.

Isolation. Filter off the dark brown-black shiny crystals, wash several times with small proportions of acetylacetone-water (1:1) and dry in *vacuo*.

Purification. Dissolve the product in the minimum volume of hot benzene and add hot petroleum ether. Cool the mixture at 0 °C.

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.

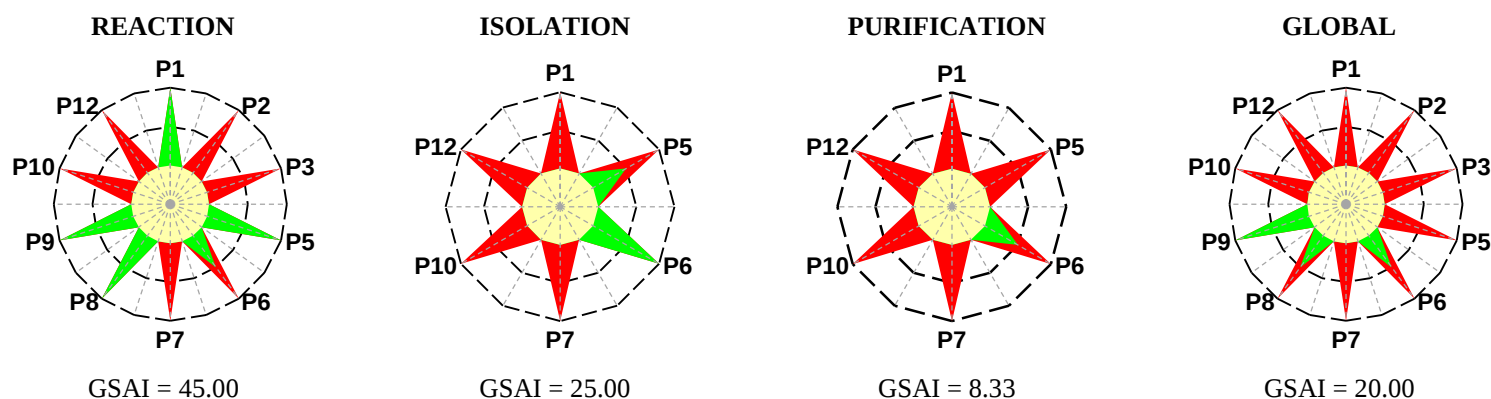


Figure 1. Greenness assessment (GS) for the synthesis of manganese(III) acetylacetonate

Construction of the GS

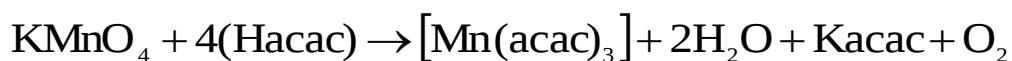


Table 1 presents the hazards and scores associated with the substances involved and Table 2 presents the scores used to construct the green stars.

Table 1. Hazards for the synthesis of manganese(III) acetylacetonate, protocol H^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
Potassium permanganate (CAS 7722-64-7)	✓			H272 (cat.2), H302, H410	2	3	3
Auxiliary substances							
Solvents							
Acetylacetone ^c (CAS 123-54-6)		✓		H226, H302	2	1	2
Benzene (CAS 71-43-2)			✓	H225, H304, H315, H319, H340, H350, H372	3	1	3
Petroleum ether (CAS 8032-32-4)			✓	H224, H304, H315, H336, H411	3	3	3
Water ^{a,b}	✓	✓		-	1	1	1
Product							
Manganese(III) acetylacetonate (14284-89-0)	✓	✓	✓	H302, H315, H319, H335	2	1	1
Waste							
Acetylacetone (excess)		✓		H226, H302	2	1	2
Benzene			✓	H225, H304, H315, H319, H340, H350, H372	3	1	3
Oxygen		✓		H270, H280	1	1	3
Petroleum ether			✓	H224, H304, H315, H336, H411	3	3	3
Potassium acetylacetonate		✓		H315, H319, H335, H361	3	1	1
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 manganese(III) acetylacetonate, protocol H^a

Green Chemistry Principle	Reaction		Isolation		Purification		Global	
	s	Explanation	s	Explanation	s	Explanation	s	Explanation
P1 Prevention	3	Without waste	1	Potassium acetylacetonate, H361	1	Benzene, H304, H340, H350, H372, and petroleum ether, H304, H411	1	Potassium acetylacetonate, H361, benzene, H304, H340, H350, H372, and petroleum ether, H304, H411
P2 Atom Economy	1	Excess of acetylacetone > 10%, formation of byproducts		NA		NA	1	Excess of acetylacetone > 10%, formation of byproducts
P3 Less hazardous chemical synthesis	1	Potassium permanganate, H410 and potassium acetylacetonate, H361		NA		NA	1	Potassium permanganate, H410, potassium acetylacetonate, H361, benzene, H304, H340, H350, H372, and petroleum ether, H304, H411
P5 Safer solvents and auxiliary substances	3	Solvents and auxiliary substances are innocuous	2	Acetylacetone-water, H302	1	Benzene, H304, H340, H350, H372, and petroleum ether, H304, H411	1	Benzene, H304, H340, H350, H372, and petroleum ether, H304, H411
P6 Increase energy efficiency	2	0 °C ≤ T ≤ 100 °C	3	Room temperature	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	1	Substances not renewable
P8 Reduce derivatives	3	One stage		NA		NA	2	Two stages
P9 Catalysts	3	Without catalysts		NA		NA	3	Without catalysts
P10 Design for degradation	1	Substances not degradable	1	Substances not degradable	1	Substances not degradable	1	Substances not degradable
P12 Safer chemistry for accident prevention	1	Potassium permanganate, H272 (cat.2), and potassium acetylacetonate, H361	1	Potassium acetylacetonate, H361	1	Benzene, H225, H304, H340, H350, H372, and petroleum ether, H224, H304	1	Potassium permanganate, H272 (cat.2), potassium acetylacetonate, H361, benzene, H225, H304, H340, H350, H372, and petroleum ether, H224, H304

^as – Score; NA – Not applicable

References

Bhattacharjee, M.N.; Chaudhuri, M.K.; Khating, D.T. Direct Synthesis of Tris (acetylacetonato)manganese(III). *J. Chem. Soc., Dalton Trans.*, **1982**, 669-670.