Supporting information

Highly Selective and Sensitive Chromogenic Detection of Nerve Agents (Sarin, Tabun and Vx): A Multianalyte Detection Approach

Vinod Kumar*, G. Raviraju, Hemlata Rana, Vepa Kameswara Rao and Arvind K. Gupta

Defence R&D Establishment, Jhansi Road, Gwalior 474002, MP, India. E-mail: *vinodpal@drde.drdo.in. Tel.: +91-751-2390203; fax: +91-751-2341148.*

Contents **Page**

1. **General Methods.** All chemicals and reagents were bought from Aldrich, Fluka and Fisher Scientific and used without further purification. All reagents for synthesis were obtained commercially and were used without further purification. Solvents such as ethanol (C_2H_5OH) and chloroform ($CHCl_3$) were purchased from S D Fine Chem. Ltd., India and dried as per the standard methods before using UV-vis spectra were recorded on a Agilent Technologies, Cary 100 UV-Vis spectrophotometer equipped with quartz cuvette (path length = 1 cm, at 25 ^oC). IR spectra were recorded on a Perkin-Elmer model BXII FTIR spectrophotometer using KBr pellets. NMR was recorded on Bruker 400 MHz Spectrometer using trimethysilane (TMS) as an internal standard Mass analysis was performed on micrOTOF-Q II of Bruker.

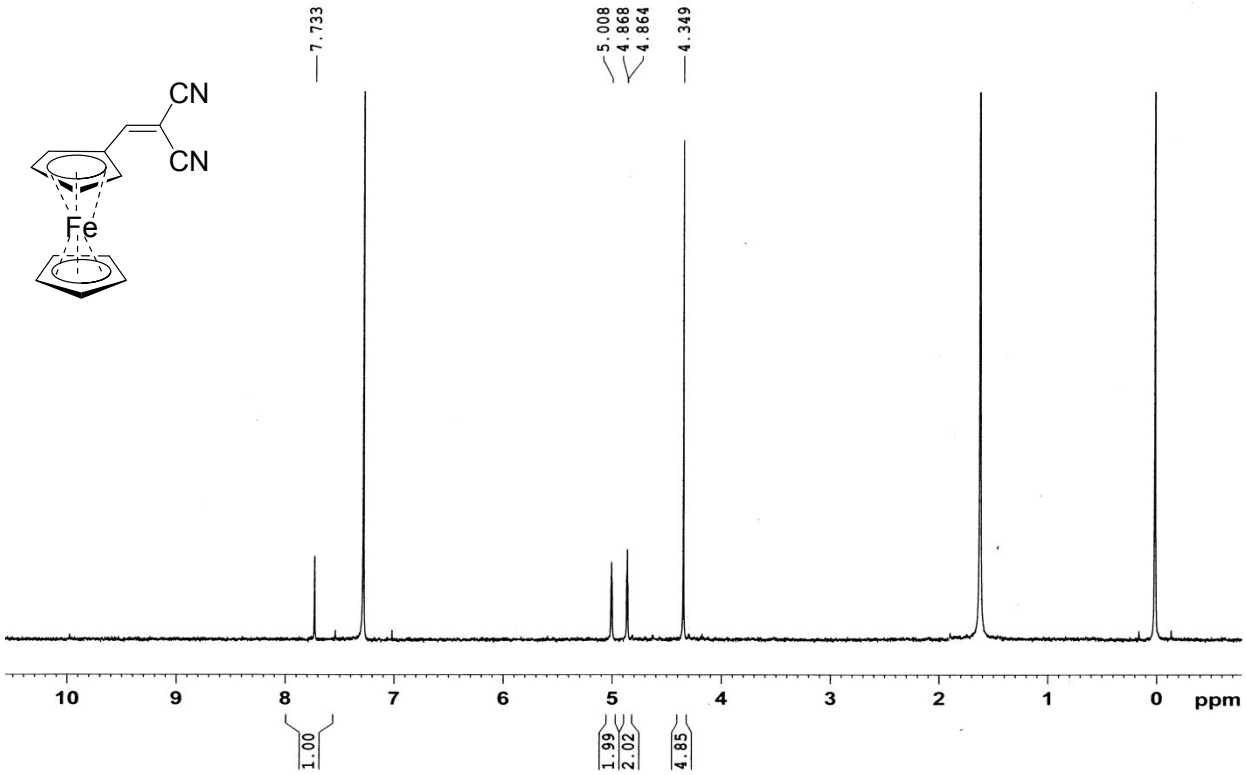
   Caution: *Nerve gents are extremely toxic in nature. Recommended operating procedure must be followed while preparing and using the chemical agents. Proper protective gears and equipments should be used while handling the agents for synthesis and analytical research).*

2. **Synthesis of 1,1-Dicyanovinyl-2-ferrocene (1).** To a solution of ferrocenecarboxyaldehyde (300 mg, 1.258 mmol) and potassium hydroxide (4.0 mg) in a mixed water:ethanol solution (4:1) (25 mL) at 50 ^oC was added malononitrile (83 mg, 1.258 mmol). The instant reaction takes place which is indicated by the formation of deep red precipitate. The reaction was stirred for 10 minutes at same temperature. The precipitate of the product formed, was filtered through sintered funnel and then washed thoroughly with cold in order to remove any substrate impurity. Melting point: 230-232 °C (uncorrected). Elemental Analysis: Calculated for $C_{14}H_{10}N_2Fe$ (262.02): C 64.18%; H 3.82%; N 10.68%; Found; C 64.1%; H 3.99%; N 10.52%; ^{1}H-NMR (400 MHz; $CDCl_3$): δ= 7.71 (s, 1H, -CH=C); 4.98 (broad s, 2H,); 4.84 (broad s, 2H); 4.33 (s, 5H, C_5H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δc: 163.1, 115.04, 114.23, 75.2, 74.06, 71.73, 71.0; IR (KBr, cm^{-1}): 2187, 2168 (CN); 1633 (C=C); 1100, 991.

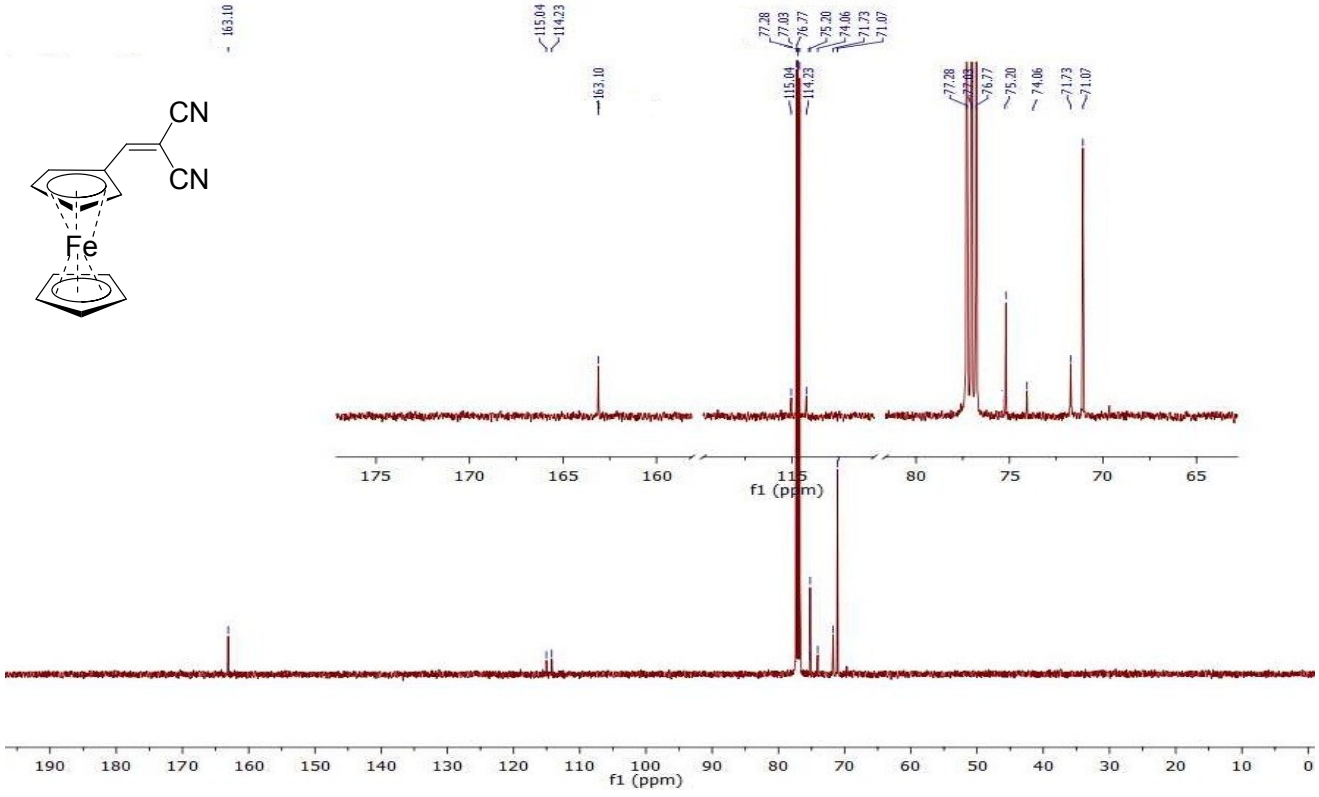
3. **Synthesis of phenylbutane-1,2,3-trione 2-oxime (2)**[1] To a solution of benzoylacetone (0.5 g, 0.0031 mol) in aqueous sulphuric acid (7%; 3.5 ml) having sufficient dioxan to give a clear solution was added sodium nitrite (0.23 g, 0.0034 mol) in water (60 ml) dropwise over 15 min at 5 ^{o}C. The reaction mixture was stirred for 1 hr at 5 ^{o}C and 1 hr at room temperature. The solution was extracted with ether (3 x 20 ml), the combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated. The residue was washed with boiling light petroleum (b.p. 40-60°), dried, and then recrystallized from benzene. Yields 50%, m.p. 124-126. The spectral data were matched with reported one[1].

4. **Synthesis of pentane-2,3,4-trione 3-oxime (3)**.[2] To a solution of 2,5-pentanedione (0.5 g, 5.0 mmol) in H_2SO_4 (1 M, 10 mL), $NaNO_2$ (0.41 g, 6.0 mmol) was added drop wise over 5 min at room temperature. The reaction mixture was stirred for another 1 hr, the product was extracted with ethyl acetate (3 × 25 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated to afford **3** (5.48 g, 85%) as a white solid; mp) 70-72 °C (lit[3] mp 75 °C); ^{1}H NMR ($CDCl_3$,): δ 10.25 (s, 1H, NOH), 2.41 (s, 3H, CH_3), 2.40 (s, 3H, CH_3).

5. ^{1}H NMR spectra of dye **1** ($CDCl_3$)



6. ^{13}C NMR spectra of dye **1** ($CDCl_3$)



7. Mass spectrum of ferrocenyl dye/CN^- Complex (ESI, -Ve mode)

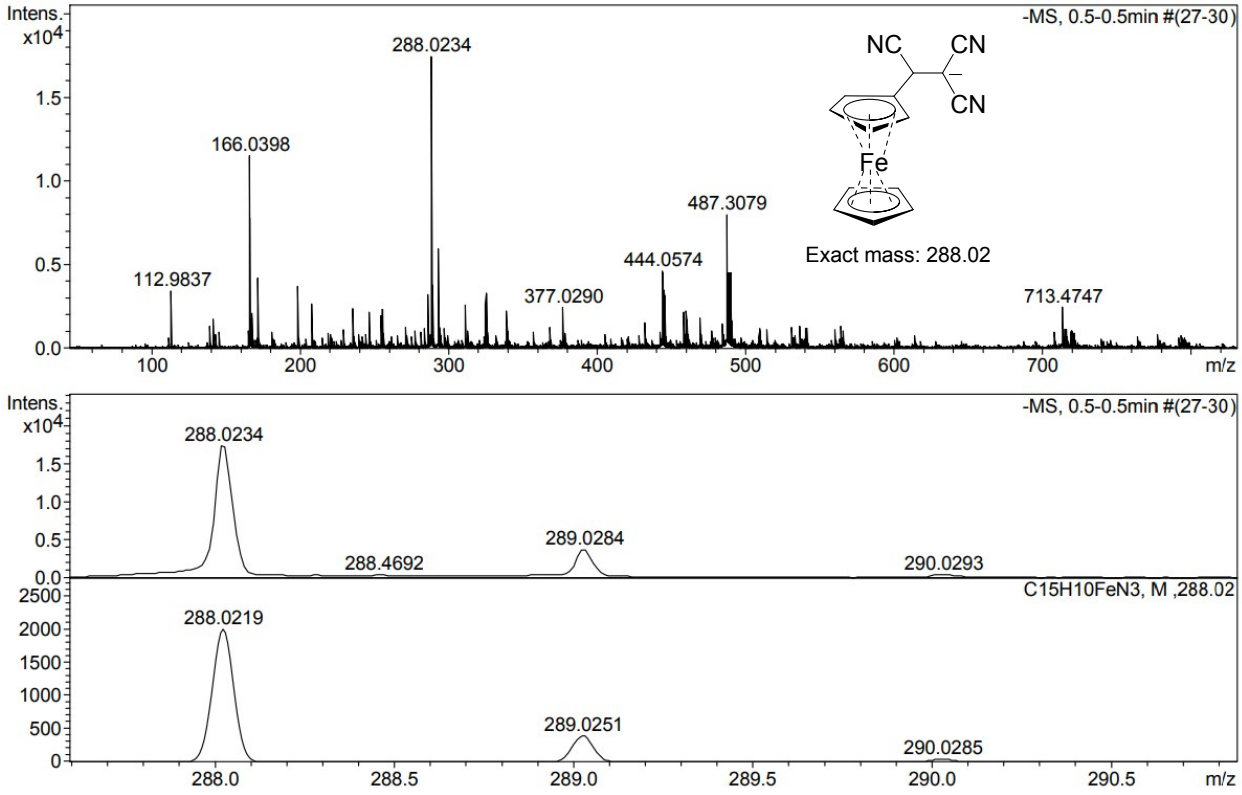


Figure S1: Mass spectrum of the ferrocenyl dye/CN complex

8. Photograph of vapor generation chamber

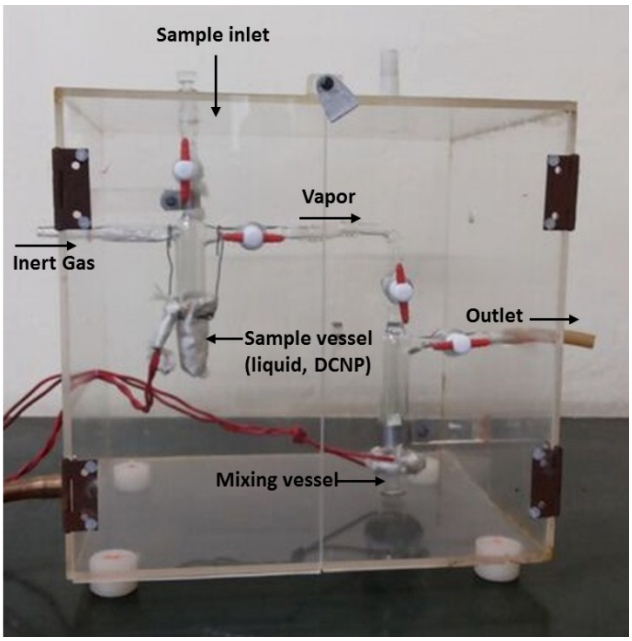


Figure S2: Vapor generation chamber

9. Chromogenic detection of Sarin and Tabun in the vapor phase.

Figure S3: Chromogenic response (from left to right) of **1** (0.29 mM) with vapours of Sarin and Tabun after 20 min of exposure.

10. Comparison of Toxicities and limits of detection (LOD) of CWAs

Table 1 | Toxicities[4] and limit of detection (LOD) of CWAs.

Nerve agents	Toxicities	Limit of detection (mg/mL)	
	LD_{50} Oral (mg/Individual)	Visual method	UV/VIS method
Tabun	25-50	0.16	0.024
Sarin	5-20	0.14	0.021
Vx	3-10	0.26	0.04

11. References:

1. B. W. Ford, P.Watts, *Journal of the Chemical Society, Perkin Transactions 2*: *Physical Organic Chemistry* **1974**, *9*, 1009.
2. T. Bark, R. P. Thummel, *Inorg. Chem*. **2005**, *44*, 8733.
3. L. Wolff, P. Bock, G. Lorentz, P. Trappe, *Ann*. **1902**, *325*, 134.
4. S. L Bartelt-Hunt, D. R. U. Knappe and M. A. Barlaz, *Cric. Rev. Environ. Sci. Tech*. 2008, **38** 112 and references therein.