Practical colorimetry of 3-nitro-1,2,4-triazol-5-one

Mat Tennant, Siao Chien Chew, Tobias Krämer[a], Nathalie Mai, Daniel McAteer[b], Jean-François Pons

Abstract: A field ready colorimetric method of quantifying the concentration of aqueous 3-nitro-1,2,4-triazol-5-one (NTO), several orders of magnitude below its environmental toxicity level, has been developed. The test allows for the immediate evaluation of the level of contamination in aqueous solution without the need for analytical equipment such as high pressure liquid chromatography (HPLC). The observed colours have been explained by the different NTO species present over the range of pH; these observations are supported by modelling and experimental results.

1 Introduction

The ongoing development of insensitive munition (IM) formulations, such as IMX-104, has seen an increase in the use and manufacture of 3-nitro-1,2,4-triazol-5-one (NTO) which is a highly water-soluble energetic material (1.3 g/100 ml at 19 °C).[1] During the industrial manufacture and processing of this explosive and its associated formulations, wastewater is contaminated with NTO at concentrations far greater than that observed with traditional explosives, which are not commonly water soluble. In addition, recent reports on the toxicity of aqueous NTO on Ceriodaphnia dubia, northern leopard frog and rat, cite toxic effects when concentrations reach and exceed the range of 1 g/l (1000 ppm), approximately one tenth of the maximum aqueous concentration.[2]

Remediation methods have been investigated for NTO contaminated wastewater.[3,4] These processes have been monitored by analytical techniques, most commonly high pressure liquid chromatography photodiode array (HPLC-PDA) or ultraviolet-visible (UV-vis) spectrometry. While HPLC-PDA and UV-vis can readily detect aqueous NTO to concentrations of less than 1 ppm, these techniques require access to a working analytical laboratory and as a result do not necessarily reflect the facilities present where NTO is being manufactured or formulated.

During investigations into the remediation of aqueous NTO, observations were made on the effect of pH on the solubility and visibility of the dissolved explosive.[3] These observations were qualified by HPLC-PDA, titration, colorimetry and UV-vis spectrometry. The UV-vis spectra were compared with calculated values and were used to suggest the species responsible for the colour of the solution. Consequently it was possible to develop a simple test method to provide immediate quantitative information on aqueous NTO several orders of magnitude below its known environmental toxicity level without the requirement for access to an analytical chemistry laboratory. This test may be used to provide a clear and immediate warning for the NTO contamination of industrially generated wastewater. The project focused on wastewater contaminated solely with NTO as it was likely to be present in aqueous concentrations which would vastly exceed

those of the other components of its associated formulations, N,N',N''-trinitro-1,3,5-triazacyclohexane (RDX), nitroguanidine (NQ) and 2,4-dinitroanisole (DNAN) (Table 1).[5]

Explosive	Solubility (g/l)
NTO	16.6
RDX	0.06
DNAN	0.28
NQ	3.8

Table 1: The reported aqueous solubility of IM formulation explosives at 25 °C[5]

2 Experimental

Aqueous NTO stock solutions were prepared, from material synthesised at Cranfield University,[6] at a concentration of 10,000 ppm (1 g/100 ml) by sonication. High purity water, prepared using the Millipore Milli Q plus purification system (18.2 MΩ.cm at 25 °C), was used for all experiments. The purity of the NTO and the concentration of the prepared solutions were validated by HPLC-PDA using a certified reference sample of NTO (AccuStandard). Basic and acidic solutions were prepared using potassium hydroxide (Analar 85 % minimum assay, BDH Chemicals) and hydrochloric acid (36 % VLSI-Selectipur, BASF).

Solubility of NTO in relation to pH

NTO was added to known volumes of water, 1M KOH and 1M HCl until saturation was achieved. The supernatant solution was sampled and the concentration determined by HPLC-PDA.

Titration of NTO

A 10 ml sample of aqueous NTO solution at 10,000 ppm was titrated against aqueous KOH 0.2 M. The pH was measured using a Kent EIL 7020 pH meter.

Ultraviolet-Visible Spectroscopy of NTO

Measurements were made using a Varian Cary 50 UV-vis spectrophotometer using a 10 mm silica glass cell. The scan was conducted between 190 and 1100 nm. A baseline spectrum was recorded for high-purity water.

Computational Methods

All electronic structure calculations were performed with the ORCA 4.0 program package.[7] Unconstrained geometry optimizations and frequency calculations were carried out at DFT level, using the TPSSh meta-hybrid exchange-correlation functional of Staroverov, Scuseria, Tao and Perdew in

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conjunction with the RIJCOSX approximation.[8,9] Dunning's correlation-consistent polarized basis set triple-ζ quality, augmented with a set of diffuse functions (aug-cc-pVTZ), was used in conjunction with the Def2/J auxiliary basis.[10,11] A tight convergence criterion was used on gradients (10–4 au) and SCF energies (10–8 au). The "Grid5/NoFinalGrid" option was employed for the DFT integration grid. Effects due to the presence of solvent were taken into account by a polarizable continuum model (CPCM), with parameters corresponding to those of water.[12] Stationary points were confirmed to be minima by the absence of imaginary frequencies. Time-dependent DFT (TD-DFT) calculations within the Tamm-Dancoff approximation were performed on the optimized geometries of the compounds. The above functional was replaced by the long-range-corrected Coulomb-attenuated B3LYP hybrid functional (CAM-B3LYP),[13] in order to account for charge-transfer excitations. The SMD solvation model (solvent water) was used for these calculations.[14]

Spot Test

Stock solutions of NTO at concentrations of 1, 10, 100, 1,000 and 10,000 ppm were prepared using high-purity water or 1M KOH. The solutions were placed in 2.5 ml glass vials and photographed under standardised lighting conditions. Averaged generic RGB codes were extracted from the resulting jpeg files using DigitalColor Meter (version 5.11, Copyright 2001-2016 Apple Inc.) and colour charts produced.

3 Results and Discussion

Solubility of NTO in relation to pH
NTO is known to be highly soluble in water, however, it was observed to increase greatly to up to 9.2 g/100 ml when dissolved in 1M KOH. In contrast, its solubility under acidic conditions (1.3 g/100 ml at pH ~ 1) is similar to literature and measured values in neutral water (Table 2).

Solvent	Maximum Concentration (g/100 ml)
1M KOH (pH 14)	9.2
Neutral deionised water (pH ~6)	1.3[1]
1M HCl (pH 1)	1.3

Table 2: Effect of pH on NTO solubility

Titration of NTO
The titration of NTO confirms its pKa ~ 3.6 and suggests a single deprotonation (observed up to 3 equivalents of KOH) occurring in aqueous media. The equivalence point at pH ~ 7.2 suggests that the increase in solubility observed at basic pH may correspond with the complete ionisation of the explosive (Figure 1).
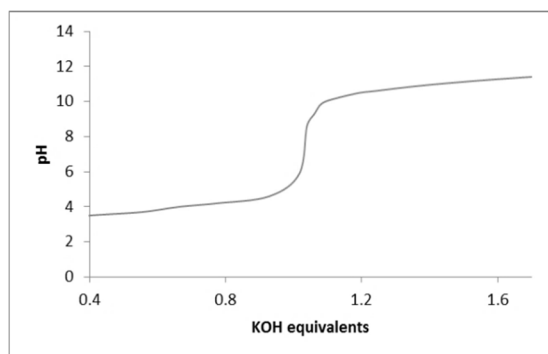

Figure 1: Titration of aqueous NTO (1 g/100 ml) with KOH

While conducting this pH titration, a gradual change of colour from pale yellow to intense orange was observed. This was confirmed by further UV-vis analyses.
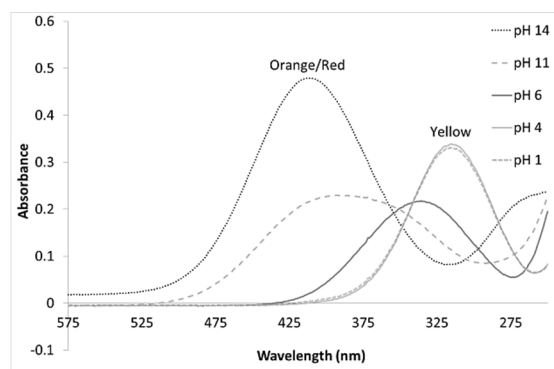

Figure 2: UV-vis spectrometry of aqueous NTO (50 ppm) at a range of pH values

Ultraviolet-Visible Spectroscopy of NTO
To accurately assess the colour change observed during the titration of NTO, UV-vis measurements were taken of solutions at a range of pH values. The concentration was limited to 50 ppm due to the intense colour seen under basic conditions, and thus absorbance. As expected, a shift in the wavelength of maximum absorbance (λmax) was detected, from 315 nm in acidic pH to 412 nm in strong basic media (Figure 2).
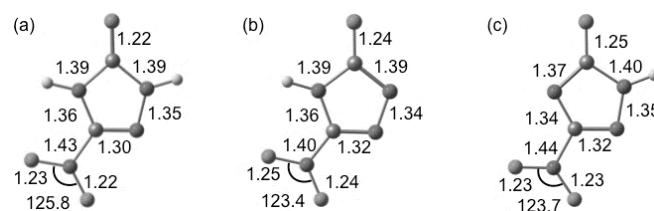

Figure 3. Optimized geometries (Å, °) of (a) NTO (b) NTO anion (tautomer A) and (c) NTO anion (tautomer B).

Calculation of coloured species

Quantum chemical calculations were utilized in order to shed light onto the chromophoric species that give rise to the observed absorptions. Optimized geometries at the CPCM(water)/TPSSh/aug-cc-pVTZ level of theory of neutral NTO and its monoanionic tautomers are depicted in Figure 3.

Optimized bond parameters are in excellent agreement with their crystallographic counterparts[15] and fall into the typical range observed for C=O, C–N, N–O and N–N bonds. Our calculations indicate that tautomer B of the anion (Figure 3) is stabilized relative to tautomer A by ΔG = 10.0 kJ mol^{-1}. This result is in line with previous theoretical studies,[16] as well as the crystallographic structures in solid state in which N4 rather than N1 is deprotonated.

Excitation energies and oscillator strengths were obtained from time-dependent (TD) DFT calculations on the optimized geometries of NTO and its anion (tautomer B). To this end, the CAM-B3LYP functional was used in conjunction with an aug-cc-pVTZ basis set, while the effect of water was accounted for by invoking the SMD solvation model. The orbital splitting of the frontier orbitals along with the excitation energy of the key electronic singlet absorption is shown in Figure 4. According to the TD-DFT calculations, the first electronic singlet transition in the neutral and anionic NTO involves the HOMO and LUMO orbitals in both cases. Analysis of these π-type MOs along with the difference densities associated with the transition indicates that these π→π* transitions correspond to an intramolecular charge-transfer process that redistributes electron density between the ring moiety and the nitro group.[17] The calculated absorption energies are in excellent agreement with the experimental values of λ_{max} at pH 14 and pH 1. For neutral NTO, which will be the dominant species at pH 1, the calculated vertical excitation energy for the π-π* transition is 327.6 nm (exp.: 315 nm). For tautomer B, the singly-deprotonated species prevailing in solution at pH 14, the π→π* excitation energy is red-shifted to 408.2 nm (exp.: 412 nm). It is more convenient to use a linear energy scale for a comparison between experimental and theoretical values for excitation energies. For the present case this deviation is 0.02-0.19 eV, which falls into the common error range for DFT.[18] We have also considered the possibility of including microsolvation in our models, to account for explicit hydrogen bonding between the solute and the solvent. However, microsolvation had only little effect on the estimated excitation energies (see Supporting Information).
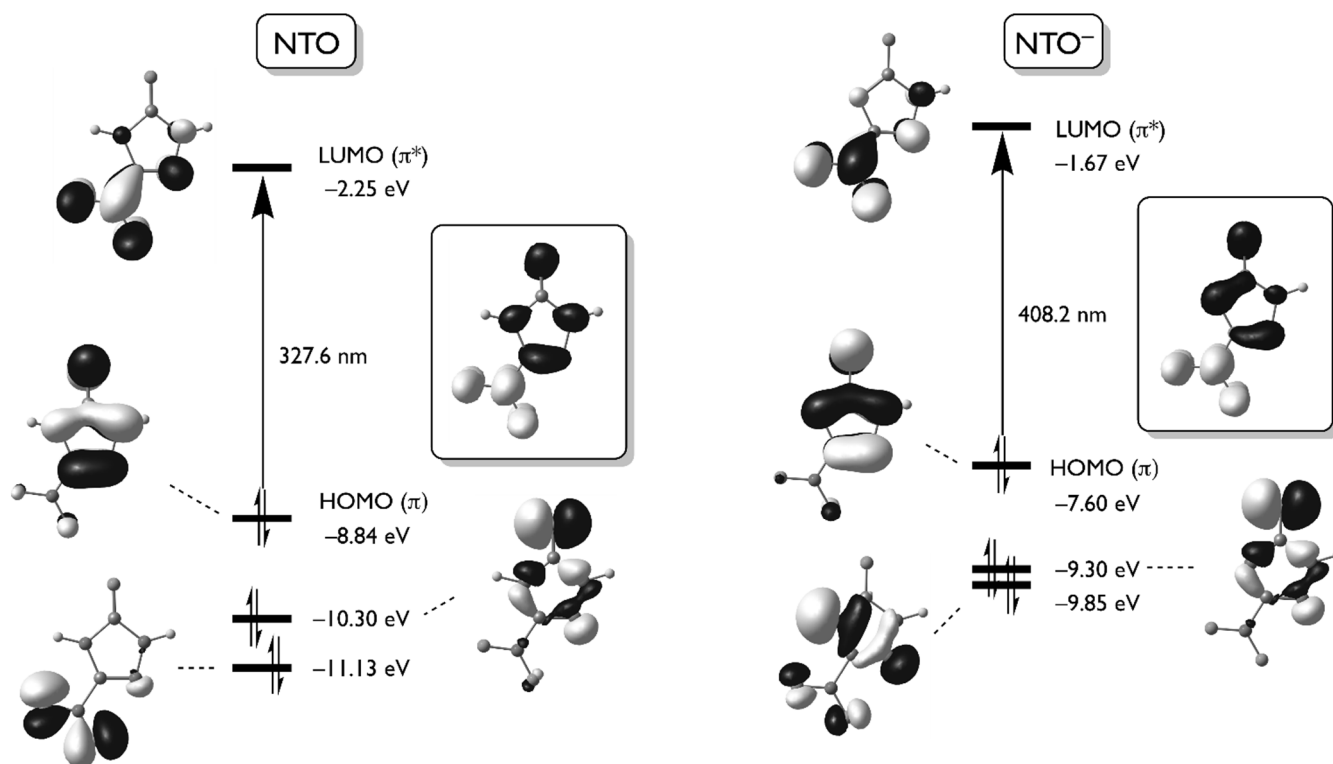

Figure 3. Frontier orbitals and energy splitting in NTO and NTO$^-$ (tautomer B). Arrows indicate the key electronic π→π* transition involving the HOMO and LUMO orbitals in both cases. Insets show plots of the difference density for these transitions (colour code: black = negative, white = positive).
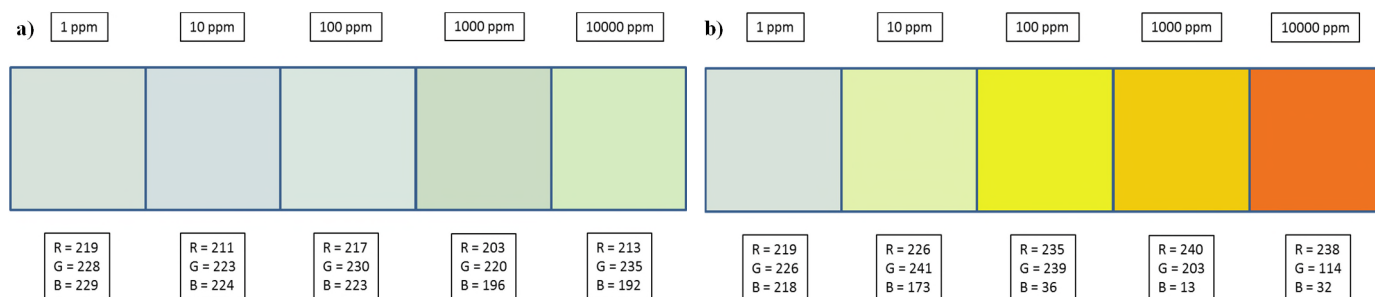
Figure 4: Colouration of NTO (average generic RGB codes included); a) in high-purity water; b) in 1M KOH.

Spot Test

The vivid colouration of the basic NTO species is visually observable from concentrations of 10 ppm. Consequently, a simple presumptive test can be used to provide a clear judgement on the presence of NTO in water and through reference to a colour chart an indication of aqueous NTO concentration may also be achieved.[19] Figure 5 shows the approximate colour of solutions of NTO in high-purity water and 1M KOH respectively.

4 Conclusions

NTO is a potential wastewater contaminant, produced during the manufacture of new IM formulations, which may be visually quantified through exposure to a base. This simple and cost-effective method of visually indicating wastewater contamination may be useful to those industries that manufacture and process NTO. This work has suggested that:

- NTO is highly soluble in aqueous base, approximately 7 times its solubility in neutral water.
- Aqueous NTO is intensely orange in colour under basic conditions and is directly visible to concentrations as low as 10 ppm, several orders of magnitude below its known toxicity range.
- The dissolved anionic NTO species is likely to be singly deprotonated at N4 as suggested by the correlation between experimental and calculated UV-vis spectra produced for a range of postulated ionic canonical forms.

5 Acknowledgements

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[19] In a clear vial, 0.5 ml of a KOH (10 M) solution is added to 4.5 ml of wastewater. Shake thoroughly and compare the colour to the chart or RGB codes provided.
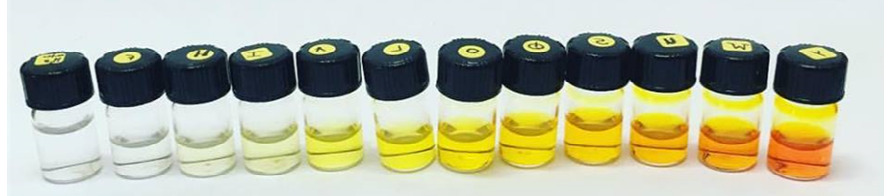
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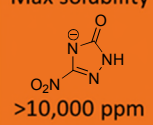
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