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ARTICLE TYPE

Doping-induced Detection and Determination of Propellant Grade Hydrazines by Kinetic Spectrophotometric Method based on Nano and Conventional Polyaniline using Halide ion Releasing Additives†

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A kinetic spectrophotometric method is described for the detection and determination of propellant grade hydrazines and its derivatives based on their reaction with 1-Chloro-2,4-dinitrobenzene (CDNB) incorporated in a solution matrix of Polyaniline-Emaraldine Base (Pani-EB) to produce HCl. This strong acid protonates (dopes) Pani (EB-Blue) to form Pani Emeraldine salt (ES-Green). Kinetic study based on the gradual decrease in absorbance at 626 nm for both nano and conventional Pani-CDNB systems was carried out at 50 °C & 60 °C under optimized conditions in the dynamic concentration range of 0.1-0.004 M. Initial rate and fixed time methods were adopted for constructing calibration curves. Hydrazines were determined based on the linear relationship between percent absorbance change at 30 min. and their concentration. R.S.D. for five replicate determinations of each one of these hydrazines using both systems is less than 1.5 %. Minimum detectable limits for hydrazines were found for both systems. This method was successfully applied for determination of hydrazines in tap water with satisfactory analytical results.

1 Introduction

Hydrazines currently used by space industries as hypergolic fuels are hydrazine, monomethylhydrazine (MMH) and UH25 (mixture of unsymmetrical dimethylhydrazine and Hydrazine Hydrate in the ratio of 75:25). They are used as propellants in missiles, space launch vehicles, satellites, auxiliary power units and small thrusters. Their use in the aircraft and space industries is dramatically increased in recent years. Because of this widespread use, toxicological properties of these compounds raise concern. Their toxicity is well known one and they are considered as potential carcinogens as they can be easily absorbed through skin[1]. In addition to hepatotoxic effects, they affect liver, kidney and brain when exposed to them. Detection and determination of these hydrazines at three concentration levels - explosive (percent), toxic and threshold limit value (TLV) levels become significant one to avoid exposure to such toxic compounds. Hence a simple and sensitive method selective to these hydrazines is required for their determination in trace amounts. Though various kinetic spectrophotometric[2-7] and flurorimetric[8] (Table 1) and fluorescence based methods[9-16] have been developed for the determination of hydrazine, they are applicable to only hydrazine and require carefully controlled test conditions. Though kinetic method developed[17] earlier by us is useful for hydrazine and MMH, they can be determined in organic medium only. The kinetic spectrophotometric method based on conjugated polymer showing the applicability not only to hydrazine but also to its derivatives such as MMH and UH25 in aqueous medium was not developed so far.

<Insert Table 1>

One of the most widely studied conjugated polymers is Polyaniline (Pani) as it is having unique property of reversible acid/base doping. It can be easily synthesized in both bulk (conventional) and nano forms which are environmentally stable. Change in the property of Pani depends on the degrees of oxidation and protonation. Upon treatment of Pani with dilute alkaline solutions, it changes into a material called emeraldine base (EB) which is blue in color. This EB form can then be protonated (doped) with a non-oxidizing protonic acid such as

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† *Electronic Supplementary Information (ESI) available: [FT-IR spectra, Percent absorbance change-Time curves, Calibration curves, Statistical data got from fixed time method and Article Reference]. See DOI: 10.1039/b000000x/*

HCl or organic acids. Doping results in the addition of a proton and counter ion for every imine nitrogen in the backbone and hence changes the EB form into ES form which is green in colour. This property change can be easily measured which makes Pani as an attractive sensor material. Pani gives a robust response to strong acids since they have the ability to fully dope the polymer resulting in very large optical property change. The changes in the structure of Pani and hence electronic absorption spectrum can be explained by the different degree of protonation of imine nitrogen atoms.

Nano structured forms of Pani such as nanofibers (Nano Pani) have recently received much attention and show promise in sensing applications. Nano Pani can be approximated as cylindrical objects which present a three-dimensional surface to potential dopants and analytes such as acid/base or oxidant/reductant. Rapid diffusion is possible into the cylindrical objects rather than into two-dimensional slabs/globules of comparable dimensions.[18]These factors are expected to be responsible for faster and larger responses to dopant exposure in nano Pani when compared with conventional Pani.

We have suggested in our earlier published review article[19] to explore the technique of adding additives into conjugated polymers (especially Pani) for detecting analytes. As part of exploring this concept, halide ion releasing additive is added to Pani which on reaction with hydrazine analyte releases reactive moiety (HX) in aqueous medium which in turn changes optical property of the polymer. In this regard, an attempt based on conductivity mode has earlier been made by S.Virji et al[20] to detect weakly acidic H_2S which are not strong enough to dope Pani. In this study, Pani (in the EB form) was mixed with a metal salt. Analyte (H_2S) reacts rapidly with metal salt to form a metal sulphide and generates a strong acid as a by-product which acts as a doping agent for Pani. It is observed that the modified Pani (with metal salt) shows very good enhancement in sensitivity on exposure to H_2S vapour. A similar approach has been demonstrated by the same group with conventional Pani for hydrazine detection using organic additives such as fluorinated alcohol[21] and amines.[22]Moreover, additives have been widely used in biosensors [23] also to increase the sensitivity of polymers. Karimi et al. and Athanasiou-Malaki et al. described halide ion releasing mechanisms by the reaction of hydrazine with N-chlorosuccinimide (chloride ion)[24] and with 1-fluoro-2,4-dinitrobenzene (fluoride ion) [25] respectively.

By utilizing the above background details, we, hereby report a kinetic spectrophotometric method for determination of hydrazines based on the change in optical property of Pani-EB which is mixed with an organic additive (1-chloro-2,4-dinitrobenzene-CDNB). Optical property change is observed when Pani-EB is exposed to HCl which is being released during the reaction between the added hydrazines and CDNB.[26] Change in the absorbance values and shifting of λ_{max} values were studied with respect to time. The level of change in the optical property depends on the amount of hydrazine in the reaction mixture and there is a linear relationship between the change in absorbance value and the amounts of hydrazines added in a particular concentration range. Therefore, this behavior allows us to develop an analytical method for the determination of hydrazines. Response time and extent of response for both nano and conventional Pani were compared. This paper deals with such a typical potential application of Pani in its nano and conventional forms as a doping induced detection material which can be used for spillage neutralization. We, herein reported linear dynamic ranges and lower detection limits for hydrazines. The method has been successfully applied for the determination of hydrazines in tap water samples and found to have satisfactory analytical characteristics as well as being applicable for environmental protection in water due to its simplicity and speed.

2 Experimental

2.1 Reagents

Aniline monomer (Merck, India) was distilled prior to use. Ammonium peroxydisulphate ($(NH_4)_2S_2O_8$ -Merck, India) was used as an oxidant. HCl was used as received as acid dopant. 1-chloro-2,4-dinitrobenzene (Sigma-Aldrich, India) was used without further purification. *N*-methyl-2-pyrrolidone (Merck, India) was used as a solvent to prepare Pani Solutions. Hydrazine (Purity: 99.8% by GC), MMH (Purity: 99.7% by GC), UH-25 (UDMH-74.4%; Hydrazine Hydrate-25.4 % by GC) are of propellant grade. Chemicals used for the spectroscopy studies were of AR grade unless otherwise specified and double distilled water was used throughout.

2.2 Synthesis

2.2.1. Synthesis of Nano Pani

Nano Pani was synthesized in an aqueous-organic two phase system. Synthetic method followed for nano pani is based on the method followed by P. Singh et al[27] with slight modification. Aniline (4 mM) was dissolved in 25 ml toluene. Ammonium peroxydisulfate (1 mM) was dissolved in 25 ml of 1M HCl solution. Both solutions were cooled to 0 °C for one hour and then carefully transferred to 60 ml reagent bottle generating an interface between the two layers. The mixed solution was kept at 0 °C for one day. After polymerization, aqueous phase was then collected, filtered and washed with distilled water till pH of 6-7 is reached. After drying at room temperature in vacuum for 12 hours, pure dark green powder was obtained. The dark green powder thus obtained was converted to Pani base by treating it with 1 M aqueous ammonium hydroxide for 12 hours. Pani base thus obtained was filtered and then dried under vacuum for 48 hours.

2.2.2. Synthesis of Conventional Pani

The synthetic method followed for conventional Pani was based on the method followed by Z. Jin et al[28] with slight modification. A solution of aniline (0.1 M) in 200 ml of 1 M HCl was cooled below 5 °C. To the above solution, Ammonium persulphate (0.15 M) in 200 ml of 1 M HCl was then added drop wise over a period of 1 hour under vigorous stirring. After 24 hours, the precipitate thus formed was collected by filtration and then washed repeatedly with 1 M aqueous HCI. The Pani hydrochloride obtained was converted to Pani Base by treatment with 1 M aqueous ammonium hydroxide. The Pani base thus obtained was dried under vacuum for 48 hours.

2.3 Characterization

Formation of Pani-EB in both nano and conventional forms was confirmed by FTIR and UV-Vis spectroscopy.

FT-IR spectra of conventional Pani in NMP medium & nano Pani (in KBr Pellet) are shown in the figures S1, S2 of ESI† respectively. UV-Vis Spectra of Pani-EB in NMP is shown in Fig.6. Information about peak maximas for both UV-Vis and FT-IR spectra are explained in ESI†.

SEM (Scanning Electron Microscope) image of the nano Pani powder (Fig.1) shows nano fibers with fiber lengths varying from 500 nm to a few microns and diameters ranging from 50 to 100 nm. Moreover, several nano particles of 25-50 nm diameters were also observed along the length of these fibers. The particles are aggregated together which may be due to several non covalent interactions like hydrogen bonds along the polymer chain.

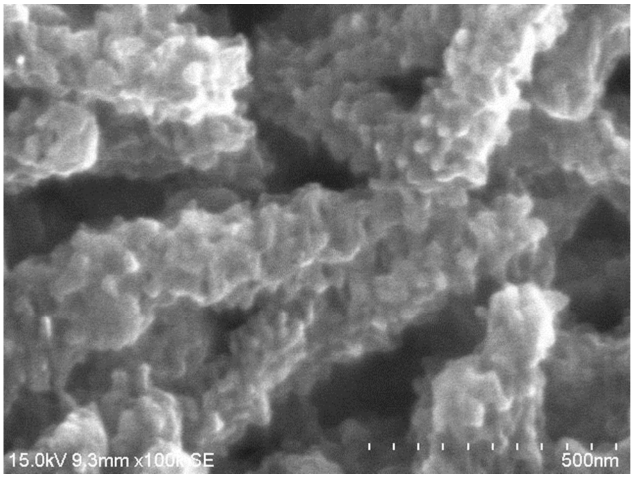

Fig. 1 SEM image of NanoPani

In contrast, SEM image of conventional Pani powder (Fig. 2) shows globular structure of 500 nm to 1 micrometer diameter. Smaller dimensions of nano Pani particles (when compared with conventional Pani particles) might be the reason for their better response towards dopants.

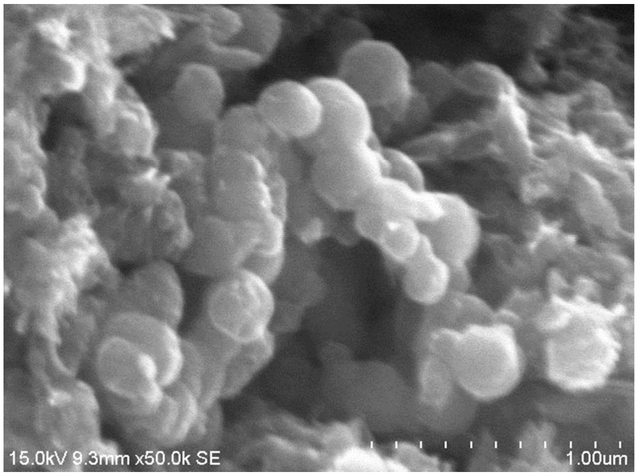

Fig. 2 SEM image of conventional Pani

As highly ordered systems can display effective response to dopants, XRD (X-ray diffraction) analyses have been performed on both forms of Pani to verify their crystalline nature. Typical XRD patterns for nano and conventional Pani were shown in Fig. 3. High intensity peaks at $2\theta = 21$ ° & 25 ° are observed in the XRD pattern of nano Pani. High intensity peaks (22 ° & 23°) are observed in XRD pattern of conventional Pani. These peaks are corresponding to (020) and (110) crystal planes of Pani. Display of broad diffraction peak corresponding to $2\theta = 23$ (in case of conventional form) and 25 (in case of nano form) is consistent with previously published data.[29]This high intensity peak at $2\theta \approx 25$ observed in both forms may be ascribed to periodicity parallel to the polymer chain. This peak represents the characteristic distance between the ring planes of benzene rings in adjacent chains or the close contact interchain distance.[30]The characteristic broadening of the observed peaks implies that both are amorphous in nature.

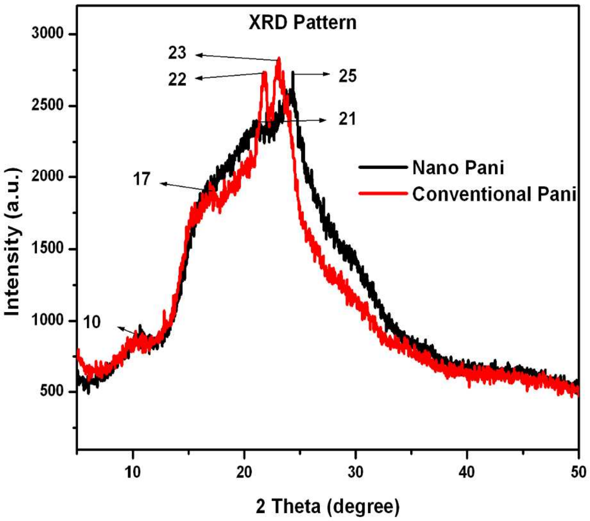

Fig. 3.XRD patterns of nano Pani and conventional Pani

3. Results and discussion

3.1. Reaction mechanism

The approach used here to enable the detection of these hydrazines is by their reaction with 1-Chloro-2,4-dinitrobenzene (CDNB) incorporated in a solution matrix of EB forms of both conventional / nano Pani to release HCl. It is well known that hydrazine and its derivatives react with CDNB to form 2,4-Dinitrophenylhydrazine and a strong acid,HCl as the by-product[26] as shown in the Fig. 4. Released HCl produces a response mechanism on Pani-EB as it gets protonated. Hence a rapid change in the optical property is observed within a short period of time. This acidic doping (shown in Fig. 5) causes a transition from Pani-EB form to Pani-ES form which is indicated by distinct colour change from blue to green.[19] As a result of protonation of the polymer backbone, bipolaron bands are formed. This has very large effects on the electronic absorption

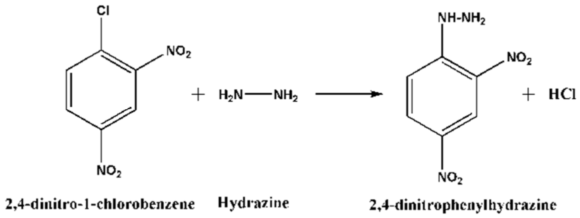

Fig.4. Reaction of hydrazine with CDNB to release HCl

spectra producing high contrast colour changes. The speed of the colour change depends on the migration speed at which the dopant ions can move in and out of the polymer matrix. When dopant ions are relatively slow moving and produced in less quantity, electrochromism of Pani will be a slow process taking about 15-30 min. for colour change to occur fully.

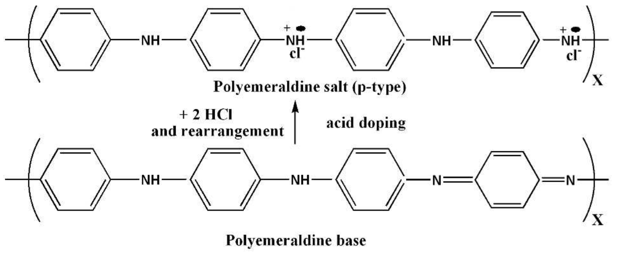

Fig.5. Conversion of Pani-EB to Pani-ES on acidic doping.

3.2. Preparation of solutions

Nano and conventional Pani sample solutions were prepared from NMP (0.1 g of sample is taken in one litre of NMP). The soluble portion is taken for further dilution to a particular concentration for which absorbance value at 626 nm is nearer to 1.0 (a.u.). Solutions of 1-Chloro-2,4-dinitrobenzene in the concentration range of 1-10 mM were prepared in NMP medium. Stock solutions of one molar Hydrazine, MMH and UH25 in double distilled water were prepared. From each stock solution, solutions with concentrations of 1, 5, 10 µM, 0.1, 0.2, 1 mM, 0.004, 0.01, 0.02, 0.04 and 0.1 M were prepared. The standard ASTM method for hydrazine in water (D1385-07) was used to standardize the concentration of these solutions. Spectrophotometric measurements were carried out at 458 nm for hydrazine and at 462 nm for MMH.[17] To standardize the concentrations of UDMH in UH25, AMRL-TDR-62-119 method was used.

4. Spectroscopy study of doping induced detection followed by determination of hydrazines

4.1 Scouting trials

Scouting experiments were performed with different solvents such as Tetrahydrofuran, Dimethylsulphoxide, *N*-methyl-2-pyrrolidone (NMP) and 1,4-dioxan to select the medium for the spectroscopy study. Tetrahydrofuran and *N*-methyl-2-pyrrolidone were found to be better options for carrying out the study as there was similar optical property changes occurred in these mediums. The advantage of NMP over THF is that the temperature increase up to 60 °C can be facilitated to improve response mechanism (due to high boiling point of NMP when compared with THF). Hence NMP was opted instead of THF as a medium for trials. Different reactants such as N-BromoSuccinimide (NBS),[31] N-ChloroSuccinimide (NCS)[32] and CDNB[26] were investigated as reagents for reaction with hydrazines to produce halide ion. Preliminary studies showed that CDNB is a suitable reagent for the present purpose.

UV-Vis Spectra of CDNB in NMP shows λ_{max} at 372 nm. Pani-EB (blue) in NMP shows λ_{max} at 326 nm & 626 nm.[29] When Pani-EB, CDNB and Hydrazine are added (in the same order) to determine the concentration of hydrazines, λ_{max} at 626 nm is shifted to 645 nm; λ_{max} at 326 nm is shifted to 334 nm; a new peak at 420 nm is observed. In addition, disappearance of peak at 626 nm followed by increase in absorbance at 326 nm is also observed (Fig. 6). Shifting of these wavelengths and change in absorbance are characteristics of protonated Pani which indicates the formation of the ES form.

Usually, ES form of Pani exhibits three bands, one at 330 nm (attributed to π- π* band), two bands at 430 nm and 800 nm in visible region (attributed to π-polaron band and polaron- π* band transistions).[33] As the reaction between CDNB and hydrazines proceeds (section 3.1), initial blue colour of Pani disappears and changes into green colour as shown in the inserted picture of Fig.6. This might be due to red shifting of 19 nm (from 626 to 645nm). When CDNB is mixed with Pani-EB in NMP medium to find its reactivity with Pani-EB, λ_{max} is blue shifted by 6 nm (626 nm→ 632 nm). Slight decrease in absorbance over a period of one hour (even for the raise of temperature to 60 °C) is noted.

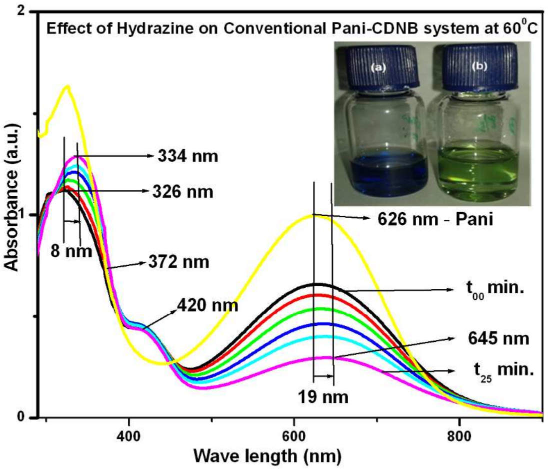

Fig. 6. UV-Vis Spectra showing the effect of hydrazine over conventional Pani-CDNB system at 60 °C. **Insert Picture:** colour change from blue to green: (a) Pani-EB in NMP (b) after the addition of 0.1 M Hydrazine at t_{25} min**.**

This shows that the reactivity between Pani-EB and CDNB is not the affecting factor for the present spectroscopy study. When water is added qualitatively in a mixture of Pani-EB and CDNB to know its effect, no change in λ_{max} and absorbance (except dilution effect) is observed. When aqueous hydrazine is added to NMP, no change in either λ_{max} or in absorbance is observed. It is to be noted that UV cut off range for N-methylpyrrolidone falls below 250 nm. When aqueous hydrazine (0.1 M) is added to Pani-EB, λ_{max} (either at 626 or 326 nm of Pani EB) is not further shifted which confirms the complete undoped nature of Pani. When hydrazine is added to CDNB, appearance of new λ_{max} at 410 nm (for which absorbance decreases over a period) and increase in absorbance value at 372 nm are observed indicating the reactivity between CDNB and hydrazine leading to the formation of Dinitrophenylhydrazine (DNPH-410 nm). Absorbance decrease at 420 nm (Fig.6) observed after the addition of hydrazine to Pani-CDNB system indicates the reaction of Dinitrophenylhydrazine with NMP leading to the formation of corresponding hydrazone which becomes colourless during the process. As the quantity of DNPH being formed in the process is very less, it is not an affecting factor in determining the concentration of hydrazines. It is to be noted that peaks at 420 nm and 410 nm could not be distinguished by UV-Vis Spectra.

In order to further understand possible structural changes of PANI induced by protonation, FTIR spectra for Pani-EB-CDNB matrix (after treatment with hydrazine) is taken in KBr medium (Fig.7.) and in NMP medium (Fig.S3 of ESI).

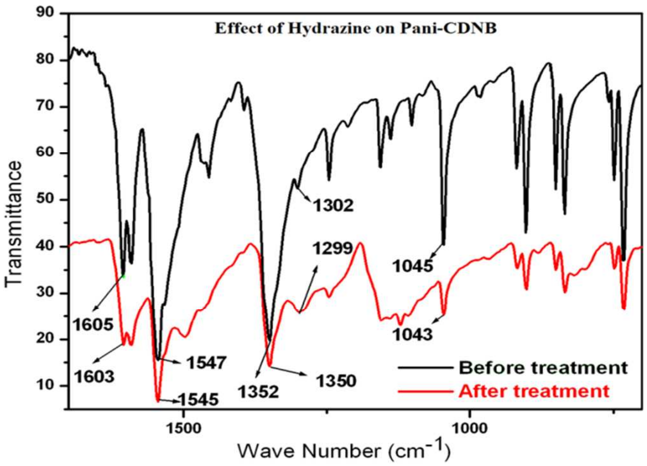

Fig. 7 FT-IR spectra indicating the effect of Hydrazine

The spectral features show that IR peaks of EB form of Pani are constantly red shifted by 2-3 cm^{-1} when it is doped by acid. The red shift is an indication of increasing degree of charge delocalization on the Pani backbone due to protonation.[34] Further to this, FT-IR spectra of Pani-ES (taken in NMP medium) formed by the release of HCl shows new peaks at 1154 and 854 cm^{-1}. Peak at 1154 cm^{-1} indicates the broken symmetry mode of the quinoid ring. The peaks at 1054 and 1014 cm^{-1} could not be seen which may be due to low doping level.[33] Peak shift of 854 cm^{-1} (out of plane bending of the aromatic ring) from 827 cm^{-1} of Pani-EB indicates the change from the quinonoid structure to the benzenoid structure upon doping.[33] It is to be noted that the solution in the final stage of individual trials appears to be yellowish green due to nature of NMP which on exposure to heat changes into light yellow.

4.2. Optimization of temperature and concentration

When Pani-EB, CDNB and Hydrazine are added in this order at room temperature (RT), shifting of λ_{max} (626 $\rightarrow$ 636 nm; 326 nm$\rightarrow$330 nm) and change in absorbance at 626 nm and 326 nm were observed but after 120 min and hence there was delay in colour change which might be due to slow rate of the reaction between CDNB and hydrazine to release HCl at RT. Hence temperature of the mixture is raised to 50 °C (from RT) using thermostatic water bath to enhance the reactivity. As the change in absorbance and color is very much enhanced at 50 °C, spectrophotometric measurements have also been carried out at 40 °C & 60 °C for comparison purpose. Spectrophotometric measurements carried out at 40° C did not provide any significant change when compared with the measurements carried out at 50 °C. As a result, measurements at 40 °C were not considered for comparison purpose.

The concentration of Pani-EB solution is so fixed that its absorbance value at 626 nm is kept at around 1.0 A. CDNB concentrations in the range of 1 mM to 10 mM are tried separately with Pani-EB solution for the effective release of HCl on addition of hydrazines. Selection of higher concentrations of CDNB (from 7 to 10 mM) leads to masking of green color with yellow as CDNB is yellow in NMP medium. Lower concentrations (from 1 to 3 mM) were not sufficient enough to release HCl for effective doping. Hence 5 mM concentration was found to be optimized one for further studies. Level of change in absorbance and colour is totally dependent on concentrations of reacting moieties namely hydrazines and CDNB which release HCl. After fixing the concentration of Pani-EB and CDNB, various concentrations of hydrazines were tried which results in absorbance change and shift in wavelength. Higher concentration of hydrazines (as there is correspondingly more release of HCl leading to higher doping level) caused swift decrease in absorbance at 626 nm and shift in wavelength. Lower concentration of hydrazines (as there is correspondingly less release of HCl leading to lower doping level) caused comparatively slow decrease in absorbance and shift in wavelength. As complete doping is not taking place, shifting of wavelength to 750 nm is not possible. Due to nature of low doping level, only decrease in absorbance is observed in almost all the trials involved in this study.

After optimizing test conditions and variables, different ratios of Pani-EB, CDNB and hydrazines (Hydrazine, MMH and UH25) were tried to establish effective change in optical property. After several trials, ratio of 2.7: 0.2: 0.6 was fixed for further experiments.

4.3. General Procedure

Into a series of 10 ml volumetric flasks were added 2.7 ml of Pani-EB (nano/conventional) solution of fixed concentration and 0.2 ml of 5 mM CDNB solution followed by 0.6 ml of Hydrazine solution (or MMH or UH25 depending on the study requirement) in the concentration range of 0.1 M to 0.004 M. The solution was mixed thoroughly and was transferred to thermo stated 1 cm quartz cell against blank. Absorbance was measured for every 5 min. during sixty minutes from the onset of the reaction. Changes in absorbance and wavelength (626 nm) were recorded with respect to time at 50 °C and 60 °C.

5. Kinetic study using nano Pani & conventional Pani at 50& 60 °C

5.1 Determination of hydrazine

In the kinetic method developed, trials were conducted on nano & conventional Pani – CDNB system (in NMP) at 50 °C & 60 °C with aqueous Hydrazine in the concentration range of 0.1 M - 0.004 M by following the general procedure stated in the section 4.3. Addition of hydrazine in this concentration range gives full colour change within 20 min and this allows one to qualitatively assess the presence of hydrazine. Periodical change in absorbance values of nano Pani-EB matrix after addition of aqueous hydrazine at 60 °C is shown in Fig. 8. Fixed time and initial rate methods were adopted for constructing the calibration curves for determining the rates of the reactions.

A. Fixed time method: Decrease in absorbance of a solution at 626 nm was recorded till pre-selected fixed time at 50 °C & 60 °C. The change in absorbance ($\Delta A=A_0-A_t$) with respect to time is converted to percent change ($\Delta A*100/A_0$) where A_0 is initial absorbance value at the start of the reaction and A_t is absorbance value at corresponding time. Out of five concentrations tried (0.1, 0.04, 0.02, 0.01 & 0.004 M), rate of the reaction increases up to 30 min for the addition of 0.1 M hydrazine (maximum concentration used in the trials) and reaches saturation level at about 30 min. This saturation level was found to be almost constant after 30 min. Therefore, calibration graphs were plotted at fixed times of 15, 20, 25 and 30 min. using percent absorbance change-time curves which are shown in Fig.S4 of ESI†.

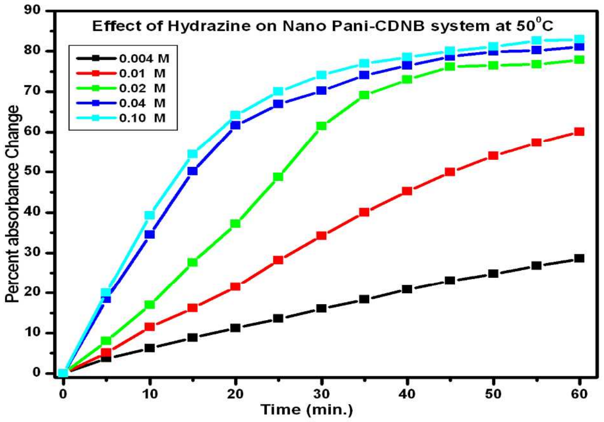

Fig. 8 Percent absorbance change-Time curves for nano Pani-CDNB system for the addition of hydrazine at different concentrations.

B. Initial rate method: Initial rate of reaction was obtained by measuring the slopes (tan α = dA/dt) of the initial tangent to the percent absorbance change-time curves obtained for the different concentrations. The data obtained by initial rate method (rate of reaction of hydrazine followed for first 15 min) is shown in the table S1, ESI†. It is apparent from the values of slope and correlation coefficient that best linearity fit was observed for the first 15 min. Based on this study, 15 min was considered for initial rate method.

For both nano Pani-CDNB and conventional-CDNB systems at 50 °C & 60 °C, rate of the reaction is increased gradually on increasing the concentration of hydrazine from 0.004 M to 0.1M. Rate difference was very less for the addition of 0.04 M and 0.1 M hydrazine. This indicates that the saturation level of hydrazine is nearing at 0.04 M for reaction with Pani-CDNB systems irrespective of temperature increase. When the temperature is increased from 50 °C to 60 °C for both of these systems, rate was found to increase by two fold for the addition of 0.004 and 0.01 M hydrazine and half fold for 0.02 M, one-third fold for 0.04 M and one-fourth fold for 0.1 M hydrazine. It is observed from the table S1 of ESI† that linearity decreases while increasing the temperature and concentration to their higher values in both systems at 50 °C & 60 °C. While comparing nano Pani system with conventional Pani system, rates of the reactions carried out at 50 °C & 60 °C are higher for nano Pani system. This might be due to very porous nature of nano fibers with small diameters and high surface area.[35,36] While the porous structure allows easy diffusion of analytes, small fiber diameters lead to rapid diffusion of dopants into Pani. Higher surface area of the nano fibers leads to faster response times. Hence nano Pani is expected to be more responsive than conventional Pani to external stimuli.

C. Analytical characteristics: ΔA is found to increase on increasing the concentration from 0.004 to 0.1 M. A linear relationship was established between percent absorbance change recorded at 30 min. and the concentration of hydrazine. Based on this observation, a new kinetic spectrophotometric method has been established for the determination of trace hydrazine. Calibration graphs of percent absorbance change noted at 30 min. versus concentrations were plotted covering the dynamic range of 0.1 M-0.004 M as shown in Fig.S5 of ESI†. The regression equations with correlation coefficients for both forms of Pani (for the trials carried out at 50 °C & 60 °C) are given in the respective curves which indicate best linearity. Minimum detection limit (MDL) obtained from practical trials is 10 μM for both nano & conventional Pani systems. Relative standard deviation (R.S.D) for five replicate determinations of 0.02 M hydrazine using nano and conventional forms of Pani at 50 °C is 0.7 and 0.9 % (Table 1) respectively. As the linearity was at its best for the trials at 50 °C when compared to trials at 60 °C, determination of all three hydrazines to find out RSD was carried out at 50 °C.

5.2. Determination of MMH

Procedure adopted for the determination of hydrazine was followed by replacing hydrazine with MMH and the observations were recorded. Addition of MMH in the concentration range of 0.004 M-0.1 M gives full colour change within 20 min and this indicates its presence. Fixed time and initial rate methods were adopted for constructing the calibration curves for determining the rates of the reactions.

A. Fixed time method: Decrease in absorbance was recorded till a preselected fixed time at 50 °C & 60 °C similar to hydrazine trials**.** Out of five concentrations tried, rate of the reaction increases up to 30 min for the addition of 0.1 M MMH and reaches saturation level at about 30 min. This saturation level was found to be almost constant after 30 min. Therefore, calibration graphs were plotted at fixed times of 15, 20, 25 and 30 min using percent absorbance change-time curves which are shown in the Fig.S6 of ESI†.

B. Initial rate method: Initial rate of reaction was obtained as stated in the section 5.1.B. The data obtained by initial rate method is shown in table S1of ESI†. Best linearity fit was observed for the first 15 min. Hence 15 min. was considered for initial rate method.

In both cases of nano and conventional Pani systems at 50 °C, & 60 °C, rate of the reaction is increased gradually on increasing the concentration of MMH from 0.004 M to 0.1 M. For the increase of temperature from 50 °C to 60 °C to nano Pani system, rate was found to increase by two fold for the addition of 0.004, 0.01 and 0.02 M MMH and two-third fold for 0.04 M, one sixth fold for 0.1 M of MMH. When the temperature is increased from 50 °C to 60 °C to conventional Pani system, rate was found to increase by two fold for the addition of 0.004 M& 0.01 M, two third fold for 0.02 M , 0.04 M & 0.1 M MMH. It is observed from the table S1 of ESI† that linearity decreases while increasing the temperature and concentration to their higher values in both cases at 50 °C & 60 °C. It is to be noted that rates of the reactions which are carried out at 50 °C to 60 °C are higher for nano Pani system when compared to conventional Pani system as expected. While comparing with the rates of hydrazine reactions, rates of MMH reactions for both nano & conventional Pani systems are higher. This might be due to faster reaction of MMH (presence of one methyl group) with CDNB when compared with hydrazine. Replacement of one hydrogen atom in hydrazine by a methyl group significantly increases its nucleophilicity. The vertical comparison of hydrazine and MMH shows that the methyl group in hydrazine activates the substituted nitrogen by factor of 11 (MMH/Hydrazine).[37]

C. Analytical characteristics: ΔA increases on increasing the concentration from 0.004 to 0.1 M.A linear relationship (similar to that of hydrazine trials) was found between percent absorbance change at 30 min. and the concentration of MMH. Hence calibration graphs of percent absorbance change recorded at 30 min. versus concentrations were plotted covering the dynamic range of 0.004 M-0.1 M as shown in Fig.S7 of ESI†. Regression equations with correlation coefficients for both forms of Pani (trials carried out at 50 °C & 60 °C) are given in the same figure. Best linearity was observed similar to hydrazine trials.

The minimum detection limit obtained from practical trials is 5 µM for both nano & conventional Pani systems. R.S.D. for five replicate determinations of 0.04M MMH by using nano Pani and conventional Pani at 50 °C are 0.4 and 0.8 % respectively (Table1). Percent change of absorbance - Time curves for the addition of MMH (0.04 M– five trials, 0.1M & 0.02 M – each one trial) to nano Pani–CDNB system at 50 °C is shown in Fig. 9.

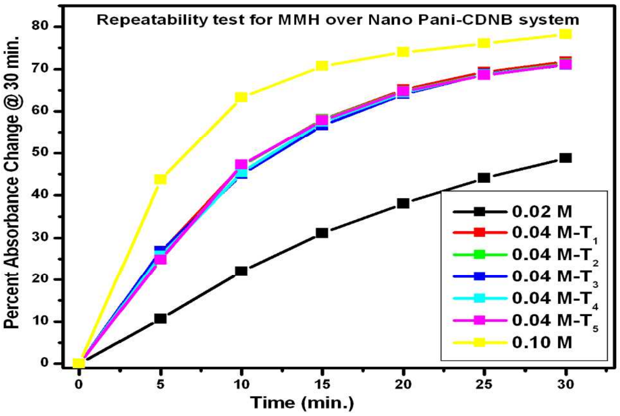

Fig.9. Percent absorbance change -Time curves for the addition of MMH (0.04 M– five trials, 0.1M & 0.02 M – each one trial) to nano Pani–CDNB system at 50 °C

5.3 Determination of UH-25:

Here, procedure adopted for the determination of hydrazine was followed by replacing hydrazine with UH-25 and the observations were recorded. Addition of UH-25 in the concentration range of 0.004M-0.1M gives full colour change within 10 min indicating its presence. As the reaction is faster when compared with hydrazine and MMH, trial with 0.001 M is also performed. Fixed time and initial rate methods were adopted for constructing the calibration curves for determining the rates of the reactions.

A. Fixed time method: Decrease in absorbance was recorded till pre-selected fixed time at 50 °C & 60 °C similar to hydrazine and MMH trials. In this case also, rate of the reaction increases up to 30 min for the addition of 0.1 M UH25 and reaches saturation level at about 30 min. This saturation level was found to be almost constant after 30 min. Therefore, calibration graphs were plotted at fixed times of 15, 20, 25 and 30 min using percent absorbance change-time curves which are shown in Fig.S8 of ESI†.

B. Initial rate method: Initial rate of reaction was obtained as stated in the section 5.1.B. The data obtained by initial rate method is shown in table S1of ESI†. As best linearity fit was observed for the first 15 min., it is considered for initial rate method.

In both cases of nano Pani and conventional Pani systems at 50 °C& 60 °C, rate of the reaction is found to increase on increasing the concentrations. Linearity is found to decrease while increasing the temperature and concentration to their higher values in both cases at 50 °C & 60 °C.

While comparing with the rates of hydrazine and MMH reactions in nano and conventional systems, rates of UDMH (present in UH25) reactions with CDNB are higher. This might be due to replacement of two hydrogen atoms by two methyl groups in hydrazine which further increases the nucleophilicity of nitrogen (when compared to MMH). The vertical comparison of UDMH and MMH shows that the methyl groups in UDMH activate the substituted nitrogen by factor of 4.9 (UDMH/MMH).[37]

In both systems, rate difference is very less on increasing the temperature from 50 °C to 60 °C. As expected, rates of the reactions of UH 25 over nano Pani system are higher than those of UH25 over conventional Pani system. This indicates that temperature increase is having very slight effect over the reactivity of UDMH present in UH25.

C. Analytical characteristics: Similar to hydrazine & MMH trials, ΔA also increases on increasing the concentration from 0.004 to 0.1 M. Calibration graphs of percent absorbance change versus concentrations were obtained covering the dynamic range of 0.001 M-0.1 M in two linear segments, 0.001 M to 0.01 M and 0.02 M to 0.1 M as shown in Fig.S9 & S10 of ESI†. The minimum detection limit obtained from practical trials is 1 µM for both nano & conventional Pani systems. R.S.D for five replicate determinations of 0.02 M of UH-25 by using nano Pani and conventional Pani at 50 °C is 0.8 and 1.2 % respectively. (Table1)

6. Application of the method

To evaluate the analytical applicability of the method, the proposed procedure was applied for determination of hydrazines in tap water. As a result, known amount (in two different trials) of hydrazine, MMH and UH25 was spiked into tap water separately. RSD for four replicate determinations of each solution using nano and conventional Pani systems at 50 °C was calculated and shown in Table S2 of ESI†. From this table, it is found that RSD for all these trials is not more than 1.5% that confirms the reliability of the proposed method. This indicates that there is no serious interference in tap water samples.

7. Salient Features of the proposed method

The following are the points observed from the experimental results for comparison between nano and conventional Pani systems.

1. Reactivity is increased in the order of hydrazine, MMH and UH25 for both nano Pani and conventional Pani systems.
2. When percent change in absorbance is nearing 30 %, the colour change (from blue to green) was observed irrespective of type of hydrazine being used. It is observed from the experiments that 50% absorbance change occurs within 10 minutes for 1 mM UH25. This indicates that UH25 was found to be the analyte with sufficient response even for lowest concentration (1 mM).
3. Linear relationship was observed between absorbance change and concentrations for all three hydrazines and this linearity decreases while increasing temperature and concentration of all the three hydrazines to their higher values.
4. For lower concentrations of Hydrazine and MMH (0.004-0.01M), rate is doubled on increasing the temperature from 50 °C to 60 °C.
5. MDL was practically found to be 10 µM for hydrazine, 5 µM for MMH and 1 µM for UH-25.
6. Relative standard deviations for five replicate determinations of one particular concentration of all three hydrazines using nano and conventional Pani systems are less than 1.5 %.
7. UH25 is found to be best analyte amongst the three hydrazines with very good response to both nano and conventional Pani systems at 50 °C & 60 °C.
8. RSD for all the three hydrazines is found to be not more than 1.5 % when spiked in tap water.

8. Conclusions

A simple mixture of solution (Pani-CDNB) for the detection of hydrazines is presented which shows distinct colour change from blue to green and used to determine hydrazines at mM concentration levels. In addition, this paper has also demonstrated that the ability and advantages of this kinetic method as a very attractive and excellent technique for the analysis of derivatives of hydrazine. This indicates the method selectivity to these analytes.

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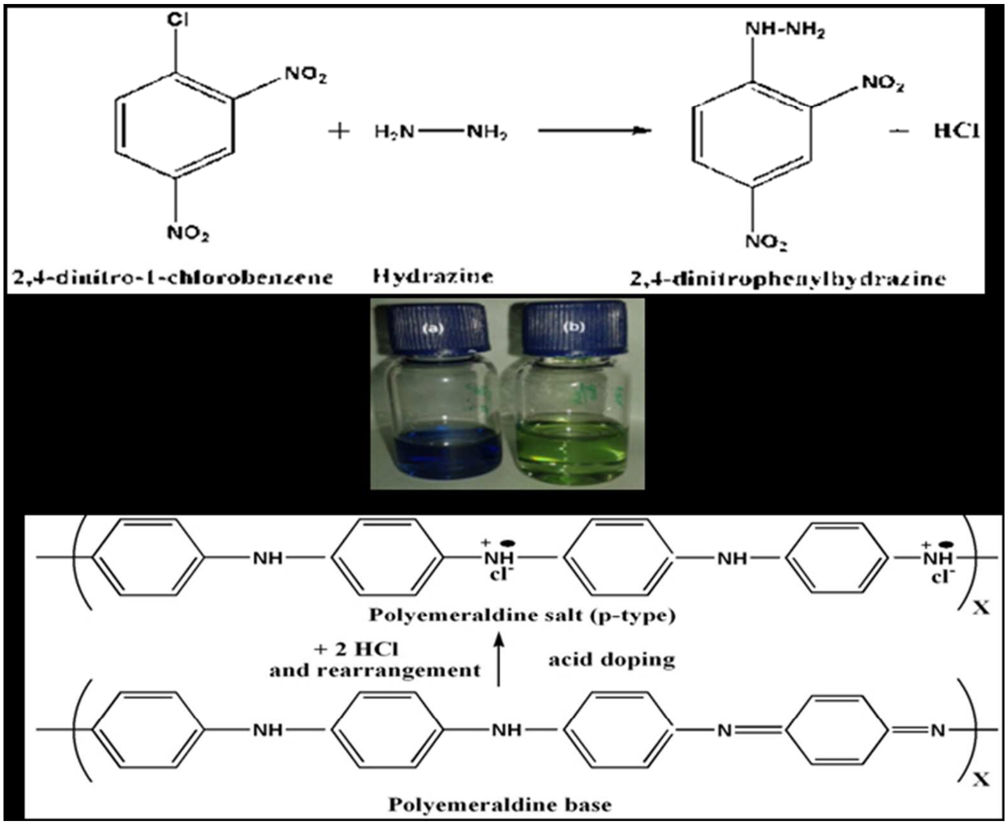
Table 1. Comparison of the proposed method with other reported kinetic methods

Reaction system	Linearity (mol/lit)	Detection Limit (mol/lit)	RSD (%) (Concentration tried, mol/lit)	Ref.
Reaction of hydrazine with Mo(VI) in hydro chloric acid medium at 30° C ; λ_{max} = 710 nm ; Time : 18 min.	1.0×10^{-4}-1.4×10^{-2}	3.1×10^{-5}	4.1 (1×10^{-5}) 2.2 (0.02) n=8	2
Inhibitory effect of hydrazine on the oxidation reaction of neutral red with nitrite in acidic media at 28° C; λ_{max} = 352 nm; Time: 6 min.	4.7×10^{-6}-3.1×10^{-5}	3.1×10^{-6}	4.0 (1.6×10^{-5}) n=10	3
Inhibitory effect of hydrazine on the oxidation of Victoria Blue 4-R by $KBrO_3$+ HCl +KCl at 20° C ; λ_{max} = 596.3 nm ; Time : 5 min.	9.4×10^{-7}-4.4×10^{-5}	10.0×10^{-8}	1.8 (3.74×10^{-5}) 8.0 (1.56×10^{-5}) n=5	4
Inhibition effect to hydrazine on Bromate-Hydrochloric acid reaction using Methyl orange; λ_{max} = 525 nm ; Time = 15 min.	3.0×10^{-7}-3.2×10^{-5}	$8.5\text{x}10^{-8}$	1.2 (1.56×10^{-6}) n=10	5
Inhibitory effect of hydrazine on the thionine-bromate system in sulfuric acid media at 25°C; λ_{max} = 601 nm ; Time : 5 min.	2.5×10^{-5}-7.2×10^{-4}	6.9×10^{-6}	0.7 (3.12×10^{-6}) n=5	6
Reducing effect of hydrazine on Iron(III) with 2,2'-bipyridine in sodium dodecyl sulfate as miscellar medium at 25° C ; λ_{max} = 520 nm ; Time : 15 min.	3.1×10^{-5}-2.5×10^{-3}	2.5×10^{-5}	2.5 (1.56×10^{-5}) n=9	7
Inhibition effect of hydrazine on the reaction of potassium chlorate + hydrochloric acid with Rhodamine B at 72° C ; λ_{exi} =: 556 nm; λ_{emi} = 578 nm ; Time :7 min ;	2.5×10^{-7}-2.5×10^{-6}	5.3×10^{-8}	1.1 (0.74×10^{-6}) 0.9 (1.48×10^{-6}) n=11	8
Inhibition effect of hydrazine on the reaction of potassium bromate + potassium bromide + sulphuric acid with Rhodamine B at 40° C ; λ_{exi} = 556 nm; λ_{emi} = 578 nm ; Time : 6 min.	1.1×10^{-7}-2.5×10^{-5}	2.5×10^{-8}	4.1 (0.49×10^{-6}) 0.8 (1.97×10^{-6}) n=11	8
Doping induced reaction of Hydrazine on nano polyaniline - 1-Chloro-2,4-dinitrobenzene system at 50° C; λ_{max} = 626 nm ;Time : 30min.	4.0×10^{-3}-1.0×10^{-1}	10.0×10^{-6}	0.7 (2×10^{-2}) n=5	Present work
Doping induced reaction of Hydrazine on conventional polyaniline - 1-Chloro-2,4-dinitrobenzene system at 50° C; λ_{max} = 626 nm ; Time : 30 min.	4.0×10^{-3}-1.0×10^{-1}	10.0×10^{-6}	0.9 (2×10^{-2}) n=5	
Doping induced reaction of Monomethyl hydrazine on nano polyaniline - 1-Chloro-2,4-dinitrobenzene system at 50° C; λ_{max} = 626 nm ; Time : 30 min.	4.0×10^{-3}-1.0×10^{-1}	5.0×10^{-6}	0.4 (4×10^{-2}) n=5	
Doping induced reaction of Monomethyl hydrazine on conventional polyaniline - 1-Chloro-2,4-dinitrobenzene system at 50° C; λ_{max} = 626 nm ; Time : 30 min.	4.0×10^{-3}-1.0×10^{-1}	5.0×10^{-6}	0.8 (4×10^{-2}) n=5	
Doping induced reaction of UH-25 on nano polyaniline-1-Chloro-2,4-dinitrobenzene system at 50° C; λ_{max} = 626 nm ; Time: 30min.	4.0×10^{-3}-1.0×10^{-1}	1.0×10^{-6}	0.8 (2×10^{-2}) n=5	
Doping induced reaction of UH-25 on conventional polyaniline - 1-Chloro-2,4-dinitrobenzene system at 50° C; λ_{max} = 626 nm ; Time : 30 min.	4.0×10^{-3}-1.0×10^{-1}	1.0×10^{-6}	1.2 (2×10^{-2}) n=5	

n= No. of determinations for particular concentrations tried.



DOPING INDUCED DETECTION AND DETERMINATION OF PROPELLANT GRADE HYDRAZINES
116x95mm (150 x 150 DPI)