Propellants, Explosives, Pyrotechnics

Determination of Diphenyl Amine (DPA) Stabilizer in Propellants – A Minireview

Pankaj E. Hande*[a] and Asit Baran Samui*[b]

Abstract: There is concern about the aged propellants as the proportion of stabilizer, diphenyl amine (DPA), keeps on reducing while maintaining the propellant formulation safe. This is a very important issue as it keeps the propellant as well as the surrounding safe from any possible mishap. Therefore, the determination of residual DPA/DPA derivatives in the propellant is of utmost importance. Various attempts have been made to determine residual DPA/derivatives content in the propellant. In this review the detection methods have been compiled and analysed for their implications, detection limit and standard deviation. The methods attempted for detection comprise volumetric, chromatographic, electroanalytical, spectroscopic and thermoanalytical techniques. The volumetric method was tried in the initial attempts by adopting chemical reactions. Chromatographic methods were reported by adopting different procedures and variations. These have been discussed in details. Electroanalytical methods have become one of the important techniques to determine the residual DPA that has been discussed in detail with incorporation of various modifications. Spectroscopic methods were also deployed to determine the DPA content in the propellant. The methods, being very straight forward and clean, have been considered effective in determination. Differential scanning calorimetry has also been tried for finding the DPA content in the propellant sample by adopting different combinations, which is also incorporated for discussion in this paper.

Keywords: Diphenyl amine · Propellants · Detection · Chromatography · Electroanalytical · Spectroscopy · Differential scanning calorimetry

1 Introduction

Nitrocellulose based propellants are being used since over 100 years. Lack of precaution in storage and handling of the aged propellant may result in serious accidents (many seen in history). Various methods have been used to investigate the stability of the propellant. Diphenyl amine (DPA) is one of the most commonly used stabilizer in single, double and triple base propellants containing nitrocellulose. With time nitrocellulose gets decomposed and results in depletion of the stabilizer. Therefore, the safe life time of aged propellant is depending upon the depletion of the stabilizer. The process involved in degradation of the nitrocellulose and role of stabilizer is shown in Figure 1. Qualitative and quantitative analysis of the DPA and its nitro derivatives in aged propellants is very important and challenging at the same time.

There are many techniques used for the determination of the DPA in aged propellants. During early years of the development, volumetric and colorimetric methods were used for the determination of the DPA [1,2].

Then, chromatographic techniques like HPLC, GC and capillary electrochromatography were widely used for the DPA analysis and are still being used. Electroanalytical methods were also used for the determination of the DPA. Further, spectroscopic methods are also used for the detection of DPA such as UV vis, FTIR and fluorescence spectrophotometry.

This review article is focused on different methods used for the determination of the DPA in aged propellant and segregated accordingly. Till date there is no review article published in this field and therefore this will give a basic
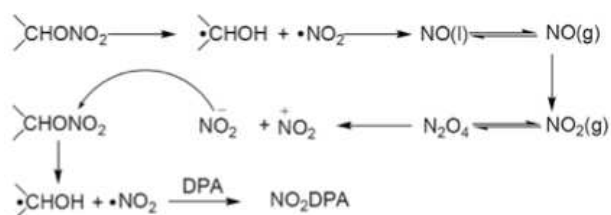

Figure 1. Process involved in degradation of nitrocellulose and effect of DPA as a stabilizer.

[a] *P. E. Hande*
Department of Chemistry,
Indian Institute of Technology Bombay,
Powai, Mumbai-400076,
India
*e-mail: pankajhande2009@gmail.com
[b] *A. Baran Samui*
Institute of Chemical Technology,
N. Parekh Marg,
Mumbai-400019, India
*e-mail: absamui@gmail.com

idea about the demand of the field. The field is still very challenging because more efficient probe for the determination of DPA is highly demanded.

2 Chromatographic Methods

Chromatography is the most prominently used technique for the separation and detection of DPA in aged propellants (Table 1). During early years for the detection of the DPA in aged propellants thin layer chromatography was used [3]. Later, high performance liquid chromatography (HPLC) has been extensively used for the detection of the stabilizer in aged propellants [4–7]. Further, the liquid chromatography in combination with the dual-amperometry was used for the detection of the DPA, 2-nitro-DPA and 4-nitro-DPA in aged propellants [8]. Furthermore, HPLC was also used for the separation and quantitative analysis of the DPA and its monoderivatives in aged single base gun propellant [9]. Two methods, viz., HPLC and heat flow calorimetry were used to evaluate the aging effect in on the triple base propellants [10]. Liquid chromatography-tandem mass spectrometry was also used for the determination of the DPA [11]. This technique was used for the determination of the DPA content along with other explosives such as trinitrotoluene, cyclotrimethylenetrinitramine, pentaerythritol

tetranitrate and nitroglycerin, respectively. For the rapid detection, GCMS is more effective and accurate than that of the by HPLC. Soxhlet extraction followed by analysis using gas chromatography and mass spectrometry were used for the determination of the propellant components [12]. Capillary electrochromatography (CEC) is the combination of the liquid chromatography and the capillary electrophoresis. Recently, CEC coupled with the UV and mass spectrometry was used for the separation and identification of the components in smokeless gun powder [13]. In another study where DPA and their derivatives in propellants were determined by the HPLC and statistical models [14]. Forced aging treatment method (65 °C for 120 days) was employed for the gun propellant containing the DPA stabilizer. Variation in time of the peak area was used to design the statistical model and used to predict the age of the propellant.

Nanostructured supramolecular solvent was used for the microextraction of the DPA and its nitro derivatives from single base propellant [15]. This solvent is was made up of nano sized inverted hexagonal aggregates of the 1-octanol. This method has low detection limit of 0.005-0.012 mg g^{-1}.

Liquid chromatography–quadrupole time-of-flight mass spectrometry was employed for detection of large number of additives in gun powders [16]. Modified tape lift device covered with a polytetrafluoroethylene (PTFE) layer was used for sample treatment instead of swabbing method

Table 1. Results of chromatography analysis of DPA-stabilizer in propellant samples.

Analytical technique	Method of Detection	Sample	LOD	RSD (%)	Ref.
HPLC	UV detection	Nitromethylaniline,[a] NDPA/[b] CDB propellant	–	–	[6]
HPLC	UV detection	DPA/[c] NC	0.5×10^{-3}–7.0×10^{-3} mg L^{-1} (0.02–0.28%)	0.04	[7]
HPLC	UV detection	DPA/Derivatives in single base gun propellant	–	–	[9]
HPLC/ calorimetry	UV detection/Heat flow calorimetry	[d] EC, akardite II, DPA,[e] MNA/Triple base propellant	–	–	[10]
LC–MS	Mass spectrometer (MS)	DPA/explosives	0.07–8.0 mg L^{-1}	6–9	[11]
GC-MS	Mass spectrometer (MS)	NC,[f] NG, DPA, Akardite II/ Double base propellant	0.8 mg L^{-1} (0.1%)	6.97–11.70	[12]
Capillary electro- chromatography (CEC)	UV/ time-of-flight (TOF)-MS	NDPA,[g] DMP,[h] MC,[i] DEP,[j] DBP,[k] NsDPA, DPA,/NG, EC,[l] DNT,	1.8 mg L^{-1} (UV), 0.6 mg L^{-1} (MS)	–	[13]
HPLC	UV/[m] DAD detection	DPA, DPA derivatives/Single and double base propellant	0.1 mg L^{-1}	–	[14]
Supramolecular solvent extraction /HPLC	UV/DAD detector	DPA, DPA derivatives/ Single base propellant	0.0166–0.04 mg L^{-1} (0.005–0.012 mg g^{-1})	4.3–10.9	[15]
LC-QTOF	Quadrupole time-of-flight (QTOF) in MS mode	DPA, MC, EC/explosives	22.40 mg L^{-1}(LOQ)		[16]
HP-TLC	UV detection	DPA, DPA derivatives, centralite, akardite/ NC	–	–	[18]

[a] NDPA- nitro diphenylamine; [b] CDB- cast double base; [c] NC- nitrocellulose; [d] EC- ethyl centralite; [e] MNA- *N*- Methyl-*p*-Nitroaniline; [f] NG-nitroglycerin; [g] DMP- dimethylphthalate; [h] MC- methyl centralite; [i] DEP- diethylphthalate; [j] DBP- dibutylphthalate; [k] NsDPA- nitro diphenylamine; [l] DNT- dinitrotoluene; [m] DAD- diode array detection.

that is less efficient. The limit of quantification (LOQ) for the DPA was 22.40 ng, and the relative standard deviation was observed to be 4.5 %. Further, calibration of DPA using this technique showed wide range linear response (100–5000 mg L^{-1}) and hence, DPA can be detected over a wide range of concentration in propellant samples.

By using GC-MS technique, the contamination of the inlet liner and any artefact formation in the firearm propellant containing DPA or others was monitored [17]. Quantitative detection of stabilizer like DPA, DPA-derivative, centralite in gunpowder was done by HP-TLC by comparing the positions of peaks and the quantitative estimation was done by comparing the area of the spot with the standard [18]. The method was used for the detection DPA in the range of 0.74–2.58 %.

The chromatographic techniques are the most widely used techniques for the determination of the DPA in aged propellant. However, but the methods are very costly, time consuming and have inability for the onsite monitoring.

3 Electroanalytical Methods

Apart from the chromatography, electrochemical methods are also used for the determination of DPA in propellants (Table 2). In early year of development in this field, a method was developed for the qualitative and quantitative analysis of the DPA in single and double based propellant based on oxidative differential pulse voltammetry with a glassy carbon electrode [19]. The concentration range accessible with this technique is 0.5–100 µM for stabilizer which is sufficient for gun propellant system. The relative standard deviation observed was 1.0–1.5 %. Cyclic voltamperograms of the DPA in acetonitrile is shown in Figure 2.

Further, the differential pulse polarography (DPP) and square wave voltammetry (SWV) were used to study the stability of the DPA and its derivatives in propellant [20]. The method was used for the determination of DPA in single base propellant system. The method showed detection limit up to 0.01 mg L^{-1}. By this method it was also possible to determine the nitro derivatives of the DPA at very low level. It was observed that the SWV is a very much effective
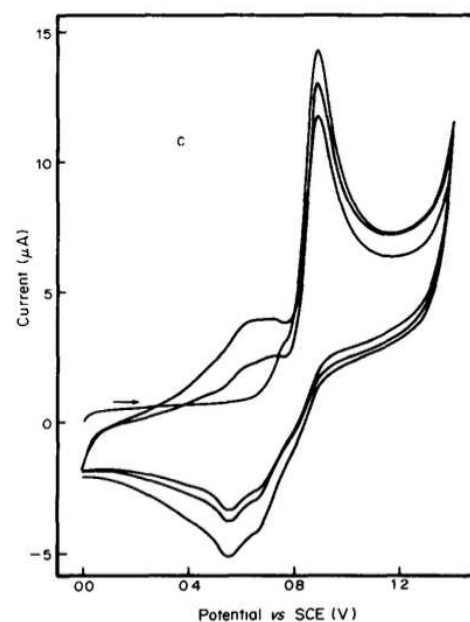

Figure 2. Cyclic voltamperograms of diphenylamine in acetonitrile. Sweep rate 100 mV s^{-1}, concentration 0.2 mM.

technique for the quantitative analysis of the DPA and its derivatives in propellant (Figure 3). The detection limit was found to be lower than that of the HPLC.

MIP technique is known for the selective recognition of the ions [21] and molecules. There are reports where MIPs are developed for the selective recognition of the DPA for various applications [22]. Recently, molecularly imprinted polymer (MIP) based carbon paste electrode sensor was developed for the detection of DPA in propellant [23]. Development of DPA-MIP and electrode sensor is shown in Figure 4. This method was used for the determination DPA in double base propellant where differential pulse voltammetry was used for the low level detection of the DPA. The probe showed detection limit of 0.1 mM for DPA. The study carried out in this work was at very preliminary level. LOD for DPA was found to be higher because of the limited accessibility of designed electrode towards DPA as the elec-

Table 2. Results of electrochemical analysis of DPA-stabilizer in propellant samples.

| Analytical technique	Method of Detection	Sample	LOD	RSD (%)	Ref.
LC with dual-Amperometry	Dual electrode amperometric detection	DPA/NC	–	–	[8]
Voltammetry	Three electrode potentiostat	Acardite II, Centralite I, DPA/ Single, Double base propellant	0.084 mg L^{-1} (0.5 µM)	1.0–1.5	[19]
Polarography/Electrochemical technique	Differential pulse polarography/Square wave voltammetry	DPA, DPA derivatives/NC propellant	0.01 mg L^{-1}	–	[20]
Electrochemical technique	Carbon paste electrode-based electrochemical sensor	DPA, Double base propellant	16.9 mg L^{-1} (0.1 mM)		[23]
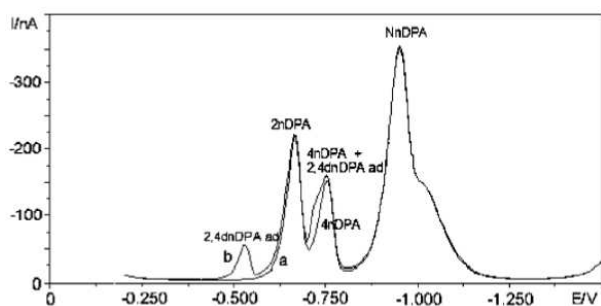
Figure 3. Square wave voltammograms of DPA and its derivatives under different conditions.
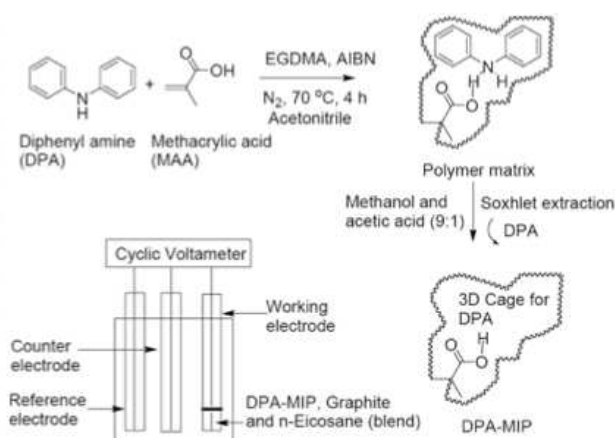

Figure 4. Designing of the electrode sensor based on DPA-MIP.

trode has very less surface area. Therefore, there is huge scope for designing highly efficient DPA probe. The electrode with high surface area like carbon paper or plate can be more effective for designing more powerful probe for detection of the DPA in aged propellant as a future scope.

Electroanalytical methods are the least explored for DPA detection in propellant as compared chromatography. But

are found to be more sensitive to DPA and therefore more powerful probe based on these methods can be realized easily. Also the electrochemical methods are found to be more efficient, cheaper, low cost and has onsite monitoring ability.

4 Spectroscopic Methods

Spectroscopic techniques, such as UV/isible, fluorescence, and Raman spectroscopy, are the most widely methods for sensing applications (Table 3). UV spectrophotometry was used for the quantitative determination of the DPA and its derivatives by oxidising them with ferric ion [24]. Upon oxidation DPA produced coloured derivative. Another simple UV-Vis spectroscopy and chemometrics techniques based method for the detection of DPA has been developed recently [25]. Analysis by UV visible spectroscopy showed strong overlapping of the spectra because of different analytes. Therefore, it was very difficult to analyse analytes in the mixture without separation and purification. To solve this problem first order UV-Vis data was carried out using the multivariate calibration method. For this, principle component regression (PCR), various modes of the partial least square (PLS), recursive weighted partial least square (rPLS), and least absolute shrinkage and selection operator (LASSO) were used for determination of DPA and its nitro-derivatives in synthetic and real samples. LASSO method gives regression coefficients (β_j) using LASSO function (1):

$$LASSO = \sum_{i=1}^{n}(y_i - \alpha - \sum_{j=1}^{p}\beta_j x_{ij})^2 + \lambda \sum_{j=1}^{p}|\beta_j| \quad (1)$$

where y is dependant and x is independent variable. n represents number of observations and p is independent variables. Furthermore, α, β_j, and λ are intercept, regression coefficients, and penalty terms, respectively.

Table 3. Results of spectroscopic analysis of DPA-stabilizer in propellant samples.

Analytical technique	Method of Detection	Sample	LOD	RSD (%)	Ref.
Spectrophotometer	Optical absorption via oxidation with ferric ion	DPA, DPA-derivatives/DNT	–	–	[24]
UV-Vis spectroscopy	Least absolute shrinkage and selection operator (LASSO) regression technique	Solid gun propellant	0.79 mg L^{-1}	8.2	[25]
FTIR	Chemometric analysis of FTIR	Single base propellant (NC, DPA)	[b] 0.2 mg g^{-1} (0.2%)	–	[26]
Near Infrared (IR)	Interpret propellant spectra using [a] biPLS algorithm	N,N-dimethyl carbanilide/Single base propellant (NC, DPA)	[b] 1.2 mg g^{-1} (1.2%)	1.38	[27]
Fluorimetry	Synchronous fluorimetry with photochemically induced fluorescence (PIF)	DPA, DPA-derivatives/ Gun powder	0.38×10^{-3} mg L^{-1} (0.38%)	1.5	[28]
Ion mobility spectrometry	+ve/-ve ion mode detection	DPA, Nitro-derivatives, EC/DNT, TNT, NG	[b] 2 ng		[29]

[b] 2 ng; [a] biPLS- backward interval partial least squares; [b] Due to the insufficient details, data could not be converted into mg L^{-1}.

Further, chemometric analysis by FTIR was also used for the detection of the stabilizer in single base propellant [26]. By this method they could determine the DPA in unknown samples up to 0.2%. This method was found to be most efficient in terms of money and time. Recently, near IR spectroscopy was used for the quantitative analysis of the DPA in single base propellant containing nitrocellulose (Figure 5) [27]. A backward interval partial least squares algorithm was used to obtain optimum pre-processing methods and efficient wavenumber region. This method gave accurate model for the quantitative measurement of the DPA in propellant.

A synchronous fluorimetry and photochemically induced fluorescence (PIF) were used for the determination of the DPA and its derivatives [28]. DPA and its derivatives shows PIF in solvent like water, methanol and acetonitrile after irradiating with the UV light. But the emission behaviour of the all these DPA derivatives overlaps with each other. Therefore, synchronous fluorometry with double scan method was used for the simultaneous determination of the DPA and its nitro derivative. This method could detect DPA up to 1×10^{-8} mol L^{-1} (LOD) concentration.

Ion mobility spectrometry (IMS) was used for the detection of the DPA and its nitro derivatives in propellant [29]. IMS is an atmospheric pressure technique for gaseous phase analytes where in presence of the electric field ion get separated with an inert gas as a mobile phase. Separation takes place on the basis of the size to charge ratio of
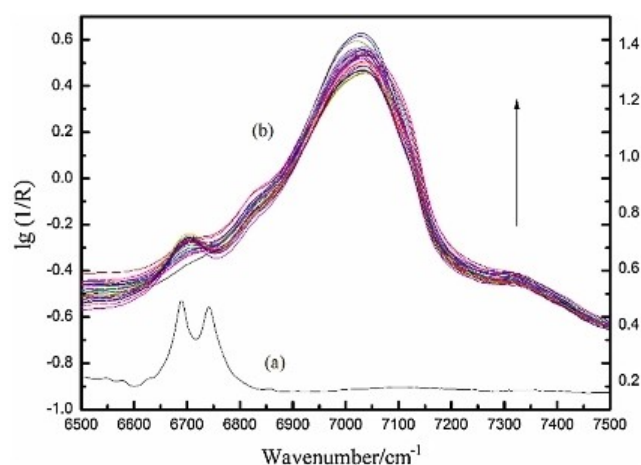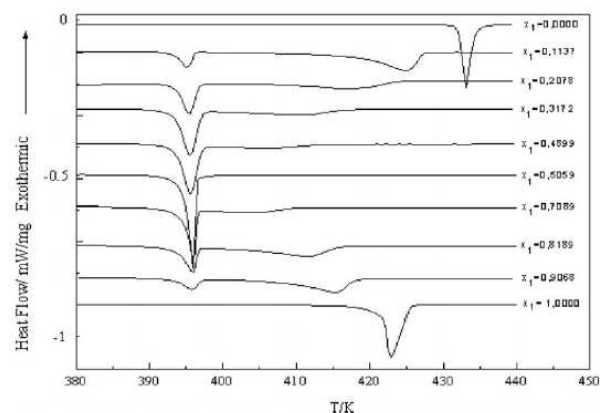

Figure 6. DSC thermogram for various compositions for 4,4'-dinitroethylcentralite and 2,4-dinitrodiphenylamine mixture.

the ions. The IMS technique was used only for the qualitative analysis of stabilizer. Therefore, for the quantitative analysis of stabilizer the IMS can be coupled with other chromatographic techniques like GC and HPLC.

5 Miscellaneous Methods

In the early years the colorimetry was tried for estimation of DPA [2] (Table 4). The lowest detection limit is around 1%. Differential scanning calorimetry (DSC) study was used to determine binary (solid + liquid) phase equilibria for four binary mixtures. The eutectic is observed as the first peak appearing at a constant temperature. The area under the eutectic peak is a function of the sample made with DPA and DPA-derivatives, centralite derivatives, nitro derivatives which are used as stabilizer in gun powders and propellants [30]. Representative DSC thermogram of the sample mixtures are shown in Figure 6. The area under the peak of eutectics are dependent on the amount and the enthalpy of the melting component. Experimental solubility results are mostly matching with the NRTL (Non-random two liquid) model. Relative standard deviation remains below 1%. The solid liquid equilibria data concerning the eutectic points of the systems is important for the stability evaluation of the gun powders and propellants.

Figure 5. NIR spectra of (a) DPA and (b) single-base propellant (DPA concentration increases along the direction of the arrow).

Table 4. Results of miscellaneous analysis of DPA-stabilizer in propellant samples.

Analytical technique	Method of Detection	Sample	LOD	RSD (%)	Ref.
Colorimetry	Color development	DPA/Nitrocellulose powder	[a] 1.01 mg g^{-1} (1.01 %)	–	[2]
Differential scanning calorimetry	Heat flow measurement	DPA, ethyl/methyl centralite, nitro DPA	–	< 1	[30]

[a] Due to the insufficient details, data could not be converted into mg L^{-1}.

6 Conclusion

Various instrumental techniques have been tried to estimate the content of various stabilizers including diphenyl amine (DPA) in a propellant formulations. After the understanding of the pathway of degradation of DPA, volumetric and colorimetric techniques have been attempted for its analysis in the early stage of determination. Later, the chromatography came in to existence and large number of studies was engaged with the determination of DPA/DPA derivatives content in the propellant mixture. Even, the lower detection limit of 0.05 mg L^{-1} was reached by using chromatography. Electroanalytical studies, including employment of MIP in the electrode matrix, were also reported with good amount of success. The spectroscopic methods were also tried for detection of DPA and its derivatives. In fact, this method is bit simpler and easy to correlate. Different multivariate calibration methods including PCR, normal PLS, and LASSO have been employed for simultaneous determination of DPA and its nitro-derivatives in synthetic as well as in real samples. The lower detection limit is 0.79 mg L^{-1}. Few miscellaneous studies are also reported, such as thermochemical and ion mobility spectrometry etc. These studies also reported quite lower detection limit (ng). Above reports on detection of propellant stabilizer is quite interesting and effective. The electrochemical analysis, HPLC and spectroscopic methods are already established. The only requirement is to modify the methods to minimize the standard deviation so that the methods can be used with confidence.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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