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SIMULTANEOUS ANALYSIS OF DIPHENYLAMINE AND ITS DERIVATIVES BY HIGH PERFORMANCE LIQUID CHROMATOGRPHY

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ABSTRACT

DPA and its derivatives always are present in propellants. They are very important components of propellants due to being quality measure of propellants. By the experimental study an analytical method based HPLC-DAD was established to determine simultaneously these compounds. All standard plot equations or standard plots of the HPLC peak area versus concentrations of DPA or its derivatives such as NO-DPA, 2- nitro –DPA, 2,4'- dinitro- DPA, 4,4'- dinitro- DPA were established. Besides, the values of LOD, LOQ of method were determined from standard plots too.

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INTRODUCTION

Diphenylamine (DPA) is an organic compound with the formula $(C_6H_5)_2NH$ used much in practice. This compound is a colorless solid, but commercial samples are often yellow due to oxidized impurities (Vogt *et al*., 2005). DPA dissolves well in many common organic solvents, and is moderately soluble in water (Conclusion on the peer review of the pesticide risk assessment of the active substance diphenylamine, 2014). DPA is used mainly for its antioxidant properties. In propellant manufacture, DPA is the most commonly used as a stabilizer of propellants, added to the propellant components in concentrations of 1-2 % (Julius, 1973 and Curtis, 1987). In the processing of preservation and storage of propellants, DPA can react with NO_2 (a product of degraded propellants) to convert in nitro-DPA derivatives such as N-nitroso-DPA, 2-nitro-DPA, 2,4' dinitro DPA and 4,4'-dinitro- DPA) (Curtis, 1987). The presence of DPA in propellants is a measure of the quality of the propellant and as propellant stabilization. Therefore, the correct determination of DPA and its derivatives in propellants would be needed. At recent time there are many methods to determine simultaneously DPA and its derivatives in propellants.

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They are gas chromatography coupled mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC) paired with the UV detector, DAD, MS and Voltammetric methods (Mathis and McCord, 2005; Jelisavac and Filipovic, 2002 Curtis, 1987). In this paper a HPLC-method determining simultaneously DPA and its derivatives in the samples was established. The method can be applied in practice to control quality of propellants.

Experimental

Chemicals

The chemicals used were of analytical reagent type (PA). They were prepared as follows: DPA (100 µg/mL in acetonitrile), N-nitroso-DPA (100 µg/mL in methanol), others such as 2,4 'dinitro DPA (99.5% purity), 2-nitro-DPA (purity 99 , 0%), (Merck- Gemany) and 4,4'-dinitro- DPA were prepared in methanol (100 µg/mL). Solvents: Methanol (MeOH) for HPLC, of 99.8% (Merck KGaA Germany), acetonitrile (ACN) for HPLC, of 99.8% (Merck KGaA Germany).

Prepare intermediate solutions:

- Solution N1, (20 µg/mL): Using the auto micro pipette, took 200µL of each original standard solution of DPA; N-

nitroso-DPA; 2 nitro-DPA; 2,4'-dinitro-DPA and 4.4 'dinitro -DPA (concentration 100µg / ml) into specialized 1,8ml bottle, mix well by an ultrasonic vibration.

- Solution N2, (10 µg/mL): Using the auto micro pipette took 200 µL of each solution N1 and 200 µL of acetonitrile solution into 1,8mL bottle, mix thoroughly by an ultrasonic vibration.
- Solution N3, (5 µg/mL): Using the auto micro pipette, taken 200 µL of each solution N2 and 200 µL of acetonitrile solution put into 1,8ml bottle, mix thoroughly by an ultrasonic vibration.
- Solution N4, (2.5 µg/mL): Using the auto micro pipette took 200µL of each solution N3 and 200µl of acetonitrile solution into 1,8mL bottle, mix well by an ultrasonic vibration.

Equipments

HPLC- DAD 1100 Instrument produced from Agilent (Mỹ) Company with column Hyspersil ODS C18(250 x 4,6mm, 5µm), and C18 (10 mm x 4,6 mm, 5 µm) and other instruments are available in the our laboratory.

Experimental procedure

Selection of column for HPLC-DAD

DPA and its derivatives are substances that exhibit the average polarization, through reference materials (Curtis, 1987; De Jong and Verweij, 1988; Yucel et al., 2011; Yucel, 2014; Chroeder, 1950, Curtis, 1987 and Nipaphan Jantama, 2008).

C18 column was selected as reversed phase to analyze DPA and derivatives. This is a common type of stationary phase, matching the conditions of the laboratory. Here the column C18 (10mm x 4,6mm, 5µm) was used for protecting and column Hypersil ODS C18 (250mm x 4,6mm, 5µm) used for separation.

- The temperature of separation column was 28^0C,
- Sample volume of 5µL, 20 µg/mL
- Flowing rate of 0.8 mL/mn.
- Detector DAD, λ = 190 - 900 nm, λ_{max} = (285, 335, 400) nm,
- Solvents: ACN-H_2O, MeOH-H_2O with different ratios

RESULTS AND DISCUSSION

The HPLC- characteristics of DPA and its derivatives in the different solvents with two components ACN (%) - H_2O (%) and MeOH (%)-H_2O (%)

The appearance of the peaks on chromatograms are present in Table 1 and Table 2. Here, the results showed that using the solvent systems with two components such as ACN-H2O and MeOH-H2O, no separation of 2,4'- dinitro-DPA and 4,4'-dinitro-DPA peaks obtained. We continued to investigate the elution peaks of DPA and derivatives by the three-component- solvent system (ACN- MeOH-H2O)

The HPLC-characteristics of DPA and its derivatives in the different solvents with three components

The results of peak- separation of DPA and its derivatives are present in Table 3. From these results, the peaks of DPA and its derivatives were fully separated when the solvent system of ACN-MeOH-H_2O with the ratio 5:60:35 was used. So this condition has been used for the further study of silmultaneous analysis of DPA and its derivatives in the samples.

The standard plot equations of DPA and its derivatives

Based on the chromatogram peaks area corresponding to the DPA and its derivative concentrations, the standard plot equations were obtained and presented in Table 4.

Table 1. Appearance of the peaks of DPA and its derivatives

Nr.	ACN (%) Vol.	H_2O (%) Vol.	Results, remarks
1	90	10	appared two peaks, they were not separated among N- Nitroso-DPA with 2,4' nitro-DPA and 2-nitro-DPA with 4,4' dinitro -DPA
2	80	20	Three 3 peaks, not separated 2,4'-dinitro-DPA and 4,4' dinitro -DPA
3	60	40	Five simple peaks, they were not clear
4	40	60	Five simple peaks, they were not clear

Table 2. Appearance of the peaks of DPA and its derivatives in MeOH-H_2O

Nr.	MeOH (% Vol.)	H_2O (% Vol.)	Results
1	90	10	Only one peak appared, it does not separate DPA and its derivatives
2	80	20	Two peaks, they do not sepaprate 2,4'-dinitro-DPA and 4,4' dinitro –DPA
3	65	35	Forth peaks but they do not separate between them.
4	40	60	Five peaks but they were not clear

Determination of LOD (Limit Of Detection) and LOQ (Limit Of Quatification) of the method.

The LOD and LOQ of method were determined basing on the standard plot equations as follows:

$$LOD = \frac{3 \times S_b}{b} \quad , \quad LOQ = \frac{10 \times S_b}{b}$$

Here S_b denoted standard derivation, b denoted slop of standard plot. By the experimental data (in Table 4), the LOD and LOQ of this method are presented in Table 5.

Table 3. Chromatograms of DPA and its derivatives in ACN- MeOH-H_2O

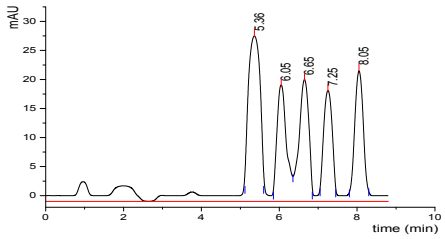
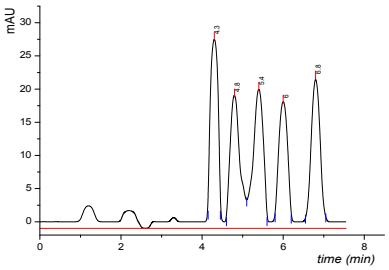
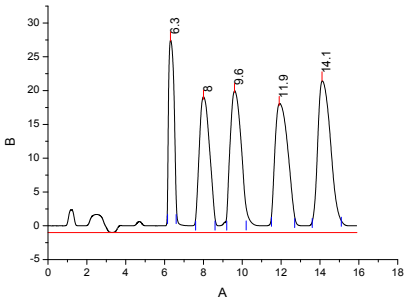
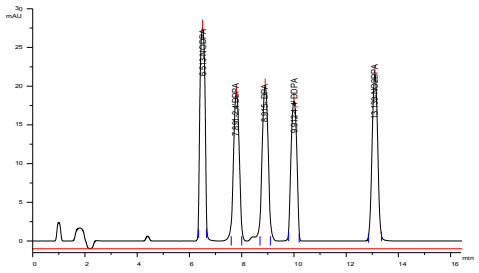
Nr.	ACN (%),Vol.	MeOH (%),Vol.	H_2O (%)Vol.	Results
1	45	20	35	 Five peaks
2	25	40	35	 Five peaks
3	10	55	35	 Five peaks.
4	5	60	35	 Five peaks.

Table 4. Standard plot equations of DPA and its derivatives

Nr.	Substances	Conc. (µg/mL)	Peak area S_{pic}	Equations
1	DPA	2.40	634.36	y = 13.103x + 591.44
		20.00	836.18	R^2 = 0.9992
		40.00	1105.84	
		80.00	1638.16	
2	Nitroso-DPA	1.20	469.76	y = 18.333x + 451.28
		12,. 0	672. 63	R^2 = 0.9999
		25.00	914.66	
		50.00	1365.19	
3	2- Nitro DPA	1.20	64.95	y = 14.8770x + 42.385
		12.00	223,16	R^2 = 0,9998
		25.00	410,56	
		50.00	787,47	
4	2,4’- dinitro DPA	0.60	37,66	y = 12.439x + 25.64
		1.0 0	44,39	R^2 = 0.9997
		12.00	172.97	
		25.00	333.84	
		50.00	649.36	
5	4,4’- dinitro DPA	0.60	9.92	y = 14.999x – 1.65
		1.20	17.85	R^2 = 0.9998
		12.00	170.51	
		25.00	375.90	
		50.00	748.81	

Table 5. LOD and LOQ of the method, (S/N = Signal to noise ratio)

Nr.	Substance	S/N	LOD (µg/mL)	LOQ (µg/mL)
1	DPA	3.15	0.725	2.39
2	NO-DPA	3.08	0.396	1.31
3	2- nitro –DPA	3.22	0.396	1.31
4	2,4'- dinitro- DPA	2.98	0.231	0.762
5	4,4'- dinitro- DPA	3.06	0.231	0.762

Conclusion

DPA and its derivatives always are present in propellants as a stabilizer. The simultaneous analysis of DPA and its derivatives was necessary. By the experimental study, an analytical method based HPLC-DAD was established that lets us simultaneously determine DPA and its derivatives such as NO-DPA, 2- nitro –DPA, 2,4'- dinitro- DPA, 4,4'- dinitro- DPA in the samples. The LOD, LOQ of DPA and its derivatives were determined.

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