Quantification of Antioxidant Nitro Derivatives: A Strategy for Optimization, Characterization, and Quantification of Antioxidant Nitro Derivatives

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ABSTRACT: As an antioxidant, N-phenyl-β-naphthylamine (PBNA) inhibits the activity of oxidants, such as NO$_2$, to prevent the degradation of energetic materials. In the presence of NO$_2$, nitro products can be generated in the process potentially. To characterize nitrated PBNA in a nontargeted analysis of complex samples as such, liquid chromatography tandem quadrupole time-of-flight (LC-QTOF), as an excellent analytic technique, is used due to its high resolution and sensitivity. However, a systematic approach of instrumentation optimization, data interpretation, and quantitative determination of products is needed. Through a step-by-step evaluation of the instrumental parameters used in the Q0, Q1, and Q2 compartments of LC-QTOF, optimal ion yields of precursor ions and high-resolution MS$^2$ fragmentation spectra at low mass defects were obtained in both negative and positive electrospray ionization modes. Through rationalization of the fragmentation pathways and verification using theoretical masses, the mononitro derivative of PBNA was accurately identified as N-(4-nitrophenyl)-naphthalen-2-amine and further confirmed using a reference standard. Using strict criteria provided by the analytical guidelines (e.g., SANTE), limit of quantitation, limit of detection, and calibration were established for the quantitation of PBNA and nitrated PBNA. From optimization to characterization and subsequent quantification of the mononitro-PBNA derivative, for the first time, the applicability of this strategy is demonstrated in the aged energetic binders.

1. INTRODUCTION

N-Phenyl-β-naphthylamine (PBNA) is a widely used antioxidant in numerous industrial applications, such as the manufacture of rubber, plastic, dyes, various greases, lubricating and transformer oils, and energetic materials. In the presence of oxidative or hydrolyzing agents such as oxygen, nitrogen oxides (NO$_x$), and nitrous and nitric acids (HNO$_x$), this secondary arylamine stabilizer can effectively protect energetic materials from oxidation or hydrolysis by scavenging the free radicals (e.g., NO$_2$ radical) and hence reducing the acidity. In a similar class of antioxidants (e.g., diphenylamine and triphenylamine), nitration of amines generally forms nitro derivatives by reacting with nitrogen oxide radicals and can be characterized using mass spectrometry (MS) through rationalization of fragmentation. Accordingly, PBNA can also form mononitro derivatives when it undergoes similar reactions. In studies of phosphite antioxidants, MS ionization is successfully employed as the primary identification method. Likewise, PBNA and its mononitro derivative can be analyzed using the electrospray ionization (ESI). However, there are three major challenges: (1) due to the inductive and resonance effects, substitution of hydrogen by NO$_2$ can decrease the acidity constant (pKa) of the polycyclic compounds. Since the concentration of PBNA is extremely low, and extraction may destroy valuable unknown products in the aged energetic binders. (2) There is a lack of literature concerning the LC-QTOF analysis of PBNA activity in energetic binders. Hence, the development of an optimal analytical method is critical to accurately determine the concentration of PBNA, identify its nitro derivatives, and evaluate the quality of the energetic binders. In this investigation, we explored various instrumental parameters, established limits of quantitation (LOQ) for compounds of interest, and developed a characterization strategy using the mononitro derivative of PBNA in the aged energetic binders as a case study.

2. RESULTS AND DISCUSSION

2.1. pH Effect. Due to the inductive and resonance effects, substitution of hydrogen by NO$_2$ can decrease the acidity constant (pKa) of the polycyclic compounds. Since the concentration of PBNA is extremely low, and extraction may destroy valuable unknown products in the aged energetic binders. (2) There is a lack of literature concerning the LC-QTOF analysis of PBNA activity in energetic binders. Hence, the development of an optimal analytical method is critical to accurately determine the concentration of PBNA, identify its nitro derivatives, and evaluate the quality of the energetic binders. In this investigation, we explored various instrumental parameters, established limits of quantitation (LOQ) for compounds of interest, and developed a characterization strategy using the mononitro derivative of PBNA in the aged energetic binders as a case study.

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retention time and ionic strength of an analyte is correlated to the pKa value and can be significantly altered under the pH effect, the pH of the mobile phases was investigated to optimize chromatographic separation. In unbuffered mobile phases, both mono- and dinitro-PBNA derivatives are deprotonated, and therefore, optimal separation of retention times can be achieved. However, poor solubility of ammonium acetate in 95:5 (v/v) ACN:MeOH poses a major concern, which increases the risk of column clogging and inconsistency of retention time. Therefore, the pH is adjusted to 6.0 to maintain the balance between the solubility of ammonium acetate salt and chromatographic resolution of analytes. As a result, the retention times of 2,2-dinitropropanol (DNPOH), PBNA, mononitro-PBNA, and dinitro-PBNA were measured at 3.300, 6.400, 6.129, and 6.103 min, respectively, with a standard deviation of ±0.030 min.

2.2. Optimization of the MS Experiment. The optimization targets four components of the LC-QTOF ion path: (1) droplet ionization, (2) the ion guide at Q0, (3) mass filtration at the Q1 analyzer, (4) fragmentation at the Q2 collision cell, and separation at the TOF analyzer. Optimization of MS parameters for PBNA and its derivatives was heavily focused on ESI+ mode due their poor sensitivity and selectivity in positive ionization, as shown in Figure 1. (1) To maximize the ionization efficiency, the flow rate (FR) was reduced from 0.40 mL/min to 0.35 mL/min, the spray voltage (SV) was increased from 4500 to 5500 V, the ion source gas 1 (GS1) pressure was increased from 30 to 50 psi, and the source temperature (TEM) was increased from 100 to 250 °C. These four parameters specifically improve the desolvation rate and therefore the droplet size is reduced before entering the mass analyzer. Also, the addition of acetic acid in the mobile phases promotes ionization efficiency, and hence increases the signal responses of the targeted analytes in ESI+. (2) As a complimentary effect of the decreased FR, the risk of column overpressure is also reduced: the column pressure dropped from initial 6500 to 4750 psi. (3) By injecting a sample of 1:1 mobile phases A:B using the information-dependent acquisition (IDA) experiment, the exclusion lists of interfering ions were obtained for both ESI+ and ESI− (Table S2). To minimize these contaminants or impurities from reaching the collision cells, the exclusion lists were applied to the IDA method with a mass tolerance of 10 mDa and an intensity threshold of 500 cps. (4) While increasing the collision energy (CE) on the MS acquisition lowers the ion yields of the precursors, increasing the CE of the MS2 acquisition induces higher order of fragmentation in the MS2 spectra. Therefore, the CE of the MS1 acquisition remains unchanged (10 V) in ESI+. Furthermore, since minimal fragmentation is desired to distinguish aromatic compounds from the aliphatic compounds, only a narrow range of collision energies in the MS2 acquisition was explored, and the resultant CE of 25 V is obtained as the optimal condition for characterization of MS2 spectra in ESI+ mode (e.g., minimal presence of low intensity or insignificant fragments).

The MS parameters in ESI− were only evaluated using the nitro derivatives due to the lack of PBNA signals (Figure 2). Since the ESI− signals were two to three times stronger than fragmentation of the precursor ions. Hence, the DP was settled at 80 V. (3) By injecting a sample of 1:1 mobile phases A:B using the information-dependent acquisition (IDA) experiment, the exclusion lists of interfering ions were obtained for both ESI+ and ESI− (Table S2). To minimize these contaminants or impurities from reaching the collision cells, the exclusion lists were applied to the IDA method with a mass tolerance of 10 mDa and an intensity threshold of 500 cps. (4) While increasing the collision energy (CE) on the MS acquisition lowers the ion yields of the precursors, increasing the CE of the MS2 acquisition induces higher order of fragmentation in the MS2 spectra. Therefore, the CE of the MS1 acquisition remains unchanged (10 V) in ESI+. Furthermore, since minimal fragmentation is desired to distinguish aromatic compounds from the aliphatic compounds, only a narrow range of collision energies in the MS2 acquisition was explored, and the resultant CE of 25 V is obtained as the optimal condition for characterization of MS2 spectra in ESI+ mode (e.g., minimal presence of low intensity or insignificant fragments).

The MS parameters in ESI− were only evaluated using the nitro derivatives due to the lack of PBNA signals (Figure 2). Since the ESI− signals were two to three times stronger than
ESI+ signals to begin with, minimal changes in the instrumental parameters were required for further signal enhancement of nitro derivatives: increased GS1 from 30 to 50 psi and the decreased DP in MS acquisition from −80 V. Finally, the dwell times or accumulation times were 50 psi and the decreased DP in MS acquisition from 0 to 40 psi.

Table 1. Verification of Ions Found in the MS² Spectra

| mode | theoretical prediction | aged sample of energetic binders | reference standard, N-(4-nitrophenyl) naphthal-2-amine | standard addition of the aged sample |
|------|------------------------|---------------------------------|-------------------------------------------------|-----------------------------------|
|      | MS² ions                | predicted m/z (Da)              | observed m/z (Da)                                | mass error (ppm)                  |
|      |                        |                                 |                                                  |                                    |
| ESI⁻ | NO²⁻                   | 45.9935                         | 45.9927                                          | −17.39                            |
|      | C₆H₄NO₂⁻                | 233.0846                        | 233.0829                                         | −7.29                             |
|      | C₆H₄NO₂O⁻               | 261.0550                        | 261.0581                                         | 0.38                              |
|      | C₆H₄NO₂O₂⁻              | 263.0826                        | 263.0814                                         | −4.56                             |
| ESI⁺ | C₆H₄N⁺                  | 217.0886                        | 217.0895                                         | 4.15                              |
|      | C₆H₄NO⁺                 | 218.0964                        | 218.0966                                         | 0.92                              |
|      | C₆H₄NO₂⁺                | 248.0944                        | 248.0947                                         | 1.21                              |
|      | C₆H₄NO₂O⁺               | 265.0972                        | 265.0968                                         | −1.51                             |
|      |                         |                                 |                                                  |                                    |
|      | observed m/z (Da)       |                                 |                                                  |                                    |
|      |                        |                                 |                                                  |                                    |
| ESI⁻ | NO²⁻                   | 45.9928                         | 45.9928                                          | −15.22                            |
|      | C₆H₄NO₂⁻                | 233.085                         | 233.0829                                         | 1.72                              |
|      | C₆H₄NO₂O⁻               | 261.0668                        | 261.0681                                         | −4.6                              |
|      | C₆H₄NO₂O₂⁻              | 263.0823                        | 263.0814                                         | −1.14                             |
| ESI⁺ | C₆H₄N⁺                  | 217.0889                        | 217.0895                                         | 1.38                              |
|      | C₆H₄NO⁺                 | 218.0956                        | 218.0966                                         | −3.67                             |
|      | C₆H₄NO₂⁺                | 248.0937                        | 248.0947                                         | −2.82                             |
|      | C₆H₄NO₂O⁺               | 265.0975                        | 265.0968                                         | 1.13                              |
|      |                         |                                 |                                                  |                                    |
|      | observed m/z (Da)       |                                 |                                                  |                                    |
|      |                        |                                 |                                                  |                                    |
| ESI⁻ | NO²⁻                   | 45.9922                         | 45.9922                                          | −28.26                            |
|      | C₆H₄NO₂⁻                | 233.085                         | 233.0829                                         | −7.29                             |
|      | C₆H₄NO₂O⁻               | 261.0668                        | 261.0678                                         | −0.77                             |
|      | C₆H₄NO₂O₂⁻              | 263.0823                        | 263.0828                                         | 0.76                              |
| ESI⁺ | C₆H₄N⁺                  | 217.0887                        | 217.0887                                         | 0.46                              |
|      | C₆H₄NO⁺                 | 218.0963                        | 218.0963                                         | −0.46                             |
|      | C₆H₄NO₂⁺                | 248.0949                        | 248.0949                                         | 2.02                              |
|      | C₆H₄NO₂O⁺               | 265.0975                        | 265.0975                                         | 1.13                              |

Table 2. Verification of the Isotopic Pattern in the MS² Spectra

| isotope, ESI⁺ | observed m/z (Da) |
|---------------|-------------------|
| 266.1002      | 264.0855          |
| 266.1003      | 264.0857          |
| mass error (ppm) | −0.38            |
| observed abundance (%) | 19.44           |
| predicted abundance (%) | 18.26          |
| abundance error (%) | 6.46            |

alignment between the aged sample and the reference standard is not impacted. The retention time of mononitro-PBNA in the aged samples is averaged to 6.127 ± 0.013 min across 55 measurements, matching the retention time obtained in the calibration standards (6.115 ± 0.016 min across 105 measurements). Furthermore, the fragmentation profile of mononitro-PBNA in the aged sample displays the same fragment fingerprints when compared to the MS² spectra of the reference standard and the standard addition (Figure 5). Since the coelvents or the nearby compounds (Figure 4, bottom row) can potentially influence the fragmentation efficiency and contaminate the MS² spectra, the varying intensities of the ion peaks at m/z 265, 248, and 218 in Figure 5 (bottom row) are therefore explained.

2.4. Evaluation of Quantitative Criteria. The LOQ limits of detection (LODs), and calibration curves were established following various analytical guidelines. The average height of the matrix blank (Figure 6, bottom) is measured across a 1 min retention time window as baseline noise. Using the measured height of the reference standard CAL1 (Figure 7) as the signal, S/N ratios are calculated at 124, 6, and 25 for DNPOH, PBNA, and mononitro-PBNA, respectively. Using the known concentrations of the reference standards and the calculated S/N ratios, the LOQs and LODs are estimated given by the commonly accepted tolerances of S/
N ratios at \( \geq 10 \) and \( \geq 3 \): \(^{24,25}\) respectively, 162.00 and 49.00 ppb for DNPOH, 6.00 and 2.00 ppb for PBNA, and 1.00 and 0.30 ppb for mononitro-PBNA. As recommended by the guideline,\(^{25}\) weighted \((1/x)\) linear regressions were applied to the calibration curves of the mixed standards (Figures 8, S1, and S2). The linearities of all calibration curves are measured at a \( R^2 \) value of greater than 0.98 (Table 3). In addition to DNPOH, the accuracies or recoveries of all standards in PBNA and the mononitro derivative are within the \( \pm 20\% \) tolerance of the calibration curve.\(^{25}\) Due to poor sensitivity in the precursor ion of DNPOH \((m/z\) 149.0203), the in-source fragment ion, deprotonated 1,1-dinitroethane \((m/z\) 119.0098, \( \text{C}_2\text{H}_3\text{N}_2\text{O}_4^- \)),

Figure 4. XICs of the aged sample (left), \( N\)-(4-nitrophenyl) naphthalen-2-amine (middle), and standard addition of the aged sample (right) obtained from ESI− (top row) and ESI+ (bottom row). The isomers of mononitro derivatives are detected in ESI+ (6.500 min) but not examined in detail because the positions of NO\(_2\) addition is unknown and the reference standards are not available.

Figure 5. \( \text{MS}^2 \) spectra of the aged sample (left), \( N\)-(4-nitrophenyl) naphthalen-2-amine (middle), and standard addition of the aged sample (right) obtained from ESI− (top) and ESI+ (bottom).

Figure 6. Average height of the baseline noises: 782 cps for DNPOH (left), 131 cps for PBNA (middle), and 200 cps for mononitro-PBNA (right) in the corresponding retention time windows.
was used as the quantifier. Perhaps associated to the effect of fragmentation efficiency, most of the recovery measurements in DNPOH standards are deviated beyond the tolerance, as depicted by the subtle quadratic characteristic in Figure 8 (left). However, accuracy can be improved either by using a targeted approach (e.g., multiple reaction monitoring or MRM) and/or through internal standard correction (e.g., using compounds that exhibit similar retention time and fragmentation behavior or deuterated DNPOH), as demonstrated by the example in Figure 8 (right) and the improved R² value of 0.997 in Table 3.

### 3. CONCLUSIONS

A nontargeted LC-QTOF method was developed to analyze PBNA and its nitro derivatives in energetic binder materials for the first time. The challenges of selectivity and sensitivity, due to the complexity of the matrix and the low concentration of PBNA, respectively, were overcome through a comprehensive assessment of instrumental parameters. Based on the demonstration of characterizing mononitro-PBNA, the quality of the spectrometric information obtained (XIC, MS¹, and MS² spectra) is very promising (mass defect <10 ppm). Using the reference material of PBNA, the determination of PBNA concentration in energetic binders is achievable. Using this experimental design, the degradation study of aged energetic binders²⁶−²⁹ will be revisited: to search for and/or verify the identities of other PBNA nitro derivatives and to uncover the mechanism of antioxidants in the thermal aging process of energetic binders.

### 4. EXPERIMENTAL SECTION

#### 4.1. Reference Chemicals.

DNPOH was synthesized by David Langlois at Los Alamos National Laboratory. The PBNA standard was purchased from Sigma-Aldrich. N-(4-nitrophenyl)naphthalen-2-amine, the reference standard of the mononitro-PBNA derivative, was purchased from Aurora Fine Chemicals (San Diego, CA). All chemicals were used as received and/or as synthesized.

#### 4.2. Sample and Calibration Preparation.

To evaluate the performance (e.g., peak intensity) of the changes in LC-QTOF parameters and for the sake of brevity, only a selected few of the aged energetic binders from the thermal aging experiment²⁶−²⁹ that contains PBNA and PBNA nitro derivatives were tested, which were prepared by dissolving 3.0±0.5 mg of the aged samples in 10 mL of ACN. Stock solutions of DNPOH, PBNA, and N-(4-nitrophenyl)-naphthalen-2-amine were prepared in ACN at 4244, 239, and 1843 ppm, respectively. By diluting the stock solutions in a 10 mL volumetric flask with appropriate volume of ACN, nine calibration standards were prepared in the concentrations as described in Table S1.

#### 4.3. LC-QTOF Parameters.

Chromatographic separation was achieved on a reversed-phase (RP) LC column: Phenomenex Kinetex 2.6 μm C8 100 Å, 150 × 2.1 mm. The aqueous and organic mobile phases were 13 mM ammonium acetate at pH 6.0 in water and in 95:5 (v/v) ACN/methanol, respectively. An InfinityLab quick change inline filter (Agilent, Part No. 5067-1603) with a stainless-steel filter disk (2.1 mm I.D., 0.2 μm porosity) was used to prevent column clogging from potential particles in the mobile phases. A SecurityLINK...
PEEKsil UHPLC finger-tight fitting (Phenomenex, Part No. AJ1-2441) was used to reduce the risk of over- or undertightening and minimize the impact of dead volume to the peak shape. The autosampler was operated at room temperature. The column oven temperature was held at 40 °C.

The sample injection volumes were set to 3 μL in ESI− and 5 μL in ESI+, and a rinse method was employed with an injection volume of 10 μL of acetone after each injection to prevent carryover contamination from the needle. The details of the optimized HPLC programs are summarized in Table 4.

ESI and IDA parameters in positive and negative modes were optimized as described in Table 5. Attributes of precursor ions (e.g., isotopic masses and relative abundances) were extracted from the spectra in the first stage of the tandem mass spectrometry (MS1). Fragment ion spectra (MS2) were generated using collisionally activated dissociation (CAD) techniques at low CE. Frequency of external calibration was set to every two injections.

### Table 4. LC Parameters (ExionLC AC)

| Parameter                  | ESI−   | ESI+   |
|---------------------------|--------|--------|
| acquisition gradient:     | (0.00, 20.0, 0.35) | (3.00, 60.0, 0.35) |
| rinse gradient:           | (0.20, 0.35) | (0.01, 99.9, 0.35) |
| DP                         | 0.10/0.05 | 0.10/0.05 |
| DP range (m/z)            | 80−650/25−580 | 80−650/25−580 |
| DP (V)                    | −80 ± 5/−50 ± 5 | 80 ± 5/70 ± 5 |
| DP (V)                    | −10/−20 ± 15 | 10/25 ± 15 |
| accumulation time (s)     | 0.10/0.05 | 0.10/0.05 |
| maximum candidate ions    | 4      | 4      |
| intensity threshold (cps) | 500    | 500    |

Concentrations of mixed calibration standards (Table S1), exclusion lists of interfering ions (Table S2), and calibration curves of PBNA and mononitro-PBNA (Figures S1 and S2) are available as Supporting Information.

### Table 5. TOF MS1/MS2 Parameters (Sciex X500R)

| Parameter                  | ESI−   | ESI+   |
|---------------------------|--------|--------|
| acquisition gradient:     | (0.00, 20.0, 0.35) | (3.00, 60.0, 0.35) |
| rinse gradient:           | (0.20, 0.35) | (0.01, 99.9, 0.35) |
| DP                         | 0.10/0.05 | 0.10/0.05 |
| DP range (m/z)            | 80−650/25−580 | 80−650/25−580 |
| DP (V)                    | −80 ± 5/−50 ± 5 | 80 ± 5/70 ± 5 |
| DP (V)                    | −10/−20 ± 15 | 10/25 ± 15 |
| accumulation time (s)     | 0.10/0.05 | 0.10/0.05 |
| maximum candidate ions    | 4      | 4      |
| intensity threshold (cps) | 500    | 500    |
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Notes
The authors declare no competing financial interest.

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