



# NDMA – Optimizing Sample Recovery: The Impact of Pressure, Temperature, and Flow

## Introduction

The Orange County Water District (OCWD) currently utilizes an in-house-developed method, based on EPA 521, for monitoring N-Nitrosodimethylamine (NDMA), N-Nitrosomorpholine (NMOR), N-Nitrosodiethylamine (NDEA), and N-Nitrosodi-n-propylamine (NDPA) in drinking water, groundwater, recycled water, surface water, and wastewater using an Isotopic Dilution Analogue (IDA) technique with an automated Solid Phase Extraction (SPE) system. Improvements from EPA 521 were made when developing the in-house method, and various experiments were conducted to identify key components that impact the results of IDA recovery.

## Experimental

- The automated SPE system used for extraction is the Dionex AutoTrace 280 (Figure 1). When developing the method, we observed that cartridge drying settings had an impact on IDA recovery. Various drying times and PSI settings were tested to achieve an optimal IDA recovery.
- EPA 521 uses two separate solvents to prepare their primary dilution standard solution (PDS). The PDS's used for the calibration preparation are in methylene chloride ( $CH_2Cl_2$ ), while the sample extraction PDS's are in water. Preparation and tracking of separate PDS's can be cumbersome, OCWD sought to lessen PDS preparation time and reduce variables in the method. OCWD converted all PDS to be prepared in methanol (MeOH) to use for both calibration preparation and sample extraction.
- The solvent evaporation system used for extract concentration is a Biotage TurboVap II (Figure 2). EPA 521 procedure states to concentrate the extracts at room temperature under a gentle stream of nitrogen flow. A slow concentration setting takes time to reach final volume, we wanted a more efficient method without sacrificing recovery. During method development, the water bath was increased from 25°C to 45°C. The nitrogen flow rate was increased from a gentle stream of 1.3 L/min to a higher flow rate of 3.5 L/min.

## Method

All tests were extracted using Analyte PDS and IDA PDS made in MeOH. A Low LFB (2 ng/L), LFB 1 (10 ng/L), and LFB 2 (10 ng/L) were extracted as tests. 500 mL of sample were fortified with IDA (25 ng/L) before extraction. Target Analytes and IDAs were passed through a 2 g activated carbon cartridge. Extraction parameters and steps are in Figure 3. Extracts were eluted in  $CH_2Cl_2$  and dried in sodium sulfate. Final volume was concentrated to 1 mL using the in-house settings from Experimental III. The 6-point calibration curves used to calculate final concentrations were also prepared using the same Analyte MeOH PDS and IDA MeOH PDS, fortified directly into a final volume of 1 mL of  $CH_2Cl_2$ . Analysis was performed by a GC/MS/MS system with a high-efficiency electron ionization (EI) source. Instrument used was an Agilent 7890B GC System with a 7010B MS Triple Quad.

Figure 1. AutoTrace 280



Figure 2. TurboVap II

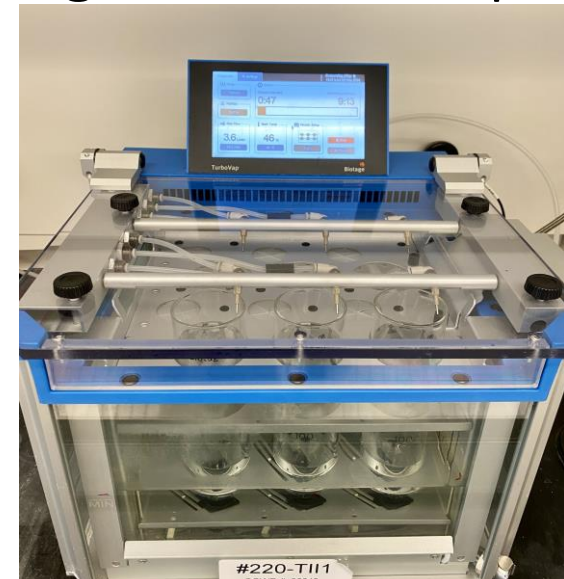


Figure 3. AutoTrace 280 extraction program. Most steps follow EPA 521, the highlighted steps are minor modifications from EPA 521.

### Parameters:

Flow Rates		SPE Parameters		Solvent Set: Standard	
Coold Flow:	1.0 mL/min	Push Delay:	1.5 sec	Solvent 1:	Methanol (CH <sub>3</sub> OH)
Load Flow:	5.0 mL/min	Air Factor:	1.0	Solvent 2:	Water (Milli-Q)
Rinse Flow:	10.0 mL/min	Autowash Vol.:	1.00 mL	Solvent 3:	N/A
Elute Flow:	3.0 mL/min	<b>Workstation Parameters</b>		Solvent 4:	Methylene Chloride (CH <sub>2</sub> Cl <sub>2</sub> )
Coold Air Push:	15.0 mL/min	Max. Elution Vol.:	12.0 mL	Solvent 5:	Methanol Rinse (CH <sub>3</sub> OH)
Rinse Air Push:	15.0 mL/min	Exhaust Fan On:	Yes		
Elute Air Push:	10.0 mL/min	Beeper On:	Yes		

### Method Steps:

Step 1.	Wash Syringe with 3.0 mL of $CH_2Cl_2$
Step 2.	Condition Cartridge with 3.0 mL of $CH_2Cl_2$ into solvent waste
Step 3.	Dry Cartridge with gas for 0.3 minutes
Step 4.	Condition Cartridge with 3.0 mL of MeOH into solvent waste
Step 5.	Dry Cartridge with gas for 0.3 minutes
Step 6.	Condition Cartridge with 3.0 mL of MeOH into solvent waste
Step 7.	Condition Cartridge with 3.0 mL of Milli-Q H <sub>2</sub> O into aqueous waste
Step 8.	Condition Cartridge with 3.0 mL of Milli-Q H <sub>2</sub> O into aqueous waste
Step 9.	Condition Cartridge with 3.0 mL of Milli-Q H <sub>2</sub> O into aqueous waste
Step 10.	Condition Cartridge with 3.0 mL of Milli-Q H <sub>2</sub> O into aqueous waste
Step 11.	Condition Cartridge with 3.0 mL of Milli-Q H <sub>2</sub> O into aqueous waste
Step 12.	Condition Cartridge with 3.0 mL of Milli-Q H <sub>2</sub> O into aqueous waste
Step 13.	<b>Pause and Alert operator, resume when Continue is pressed</b>
Step 14.	Load 530.0 mL of sample onto Cartridge
Step 15.	Dry Cartridge with gas for 10.0 minutes (AutoTrace pressure: 10 PSI)
Step 16.	Soak and Collect 5.0 mL Fraction using $CH_2Cl_2$
Step 17.	Soak and Collect 3.0 mL Fraction using $CH_2Cl_2$
Step 18.	Collect 3.0 mL Fraction into sample tube using $CH_2Cl_2$
Step 19.	<b>End. Remove Conical Collection Tubes from AutoTrace</b>

Estimated Time For 6 Samples: 2 hours : 5 min

## Results and Discussion I

IDA recovery was calculated based on the IDA response average of a non-extracted 6-point calibration curve. Lower recovery for NDMA-d6, NMOR-d8, and NDEA-d10 was observed with a 20-minute dry time (Figure 4). Improved recovery for all four IDA's was observed with a 10-minute dry time at 10 PSI and 15 PSI (Figure 4).

Figure 4. IDA % Recovery vs. Various Dry Settings



## Results and Discussion II

Accurate recovery was observed when using MeOH PDS for extraction (Figure 5a & 5b) and for calibration curve preparation (Figure 5c). Consistent calibration curve IDA response was observed using MeOH PDS (Figure 5d). Acceptable peak shape was observed for both extracted sample and direct made calibration standard (Figure 6).

Figure 5a. MeOH PDS: Extracted Analyte % Recovery Figure 5c. MeOH PDS: Calibration Curve Analyte % Recovery

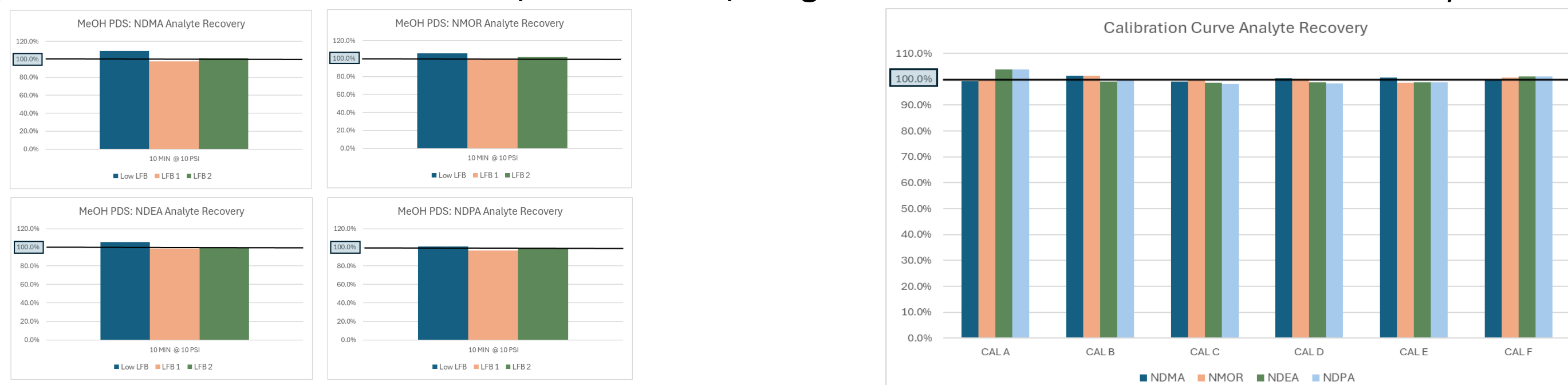


Figure 5b. MeOH PDS: Extracted IDA % Recovery

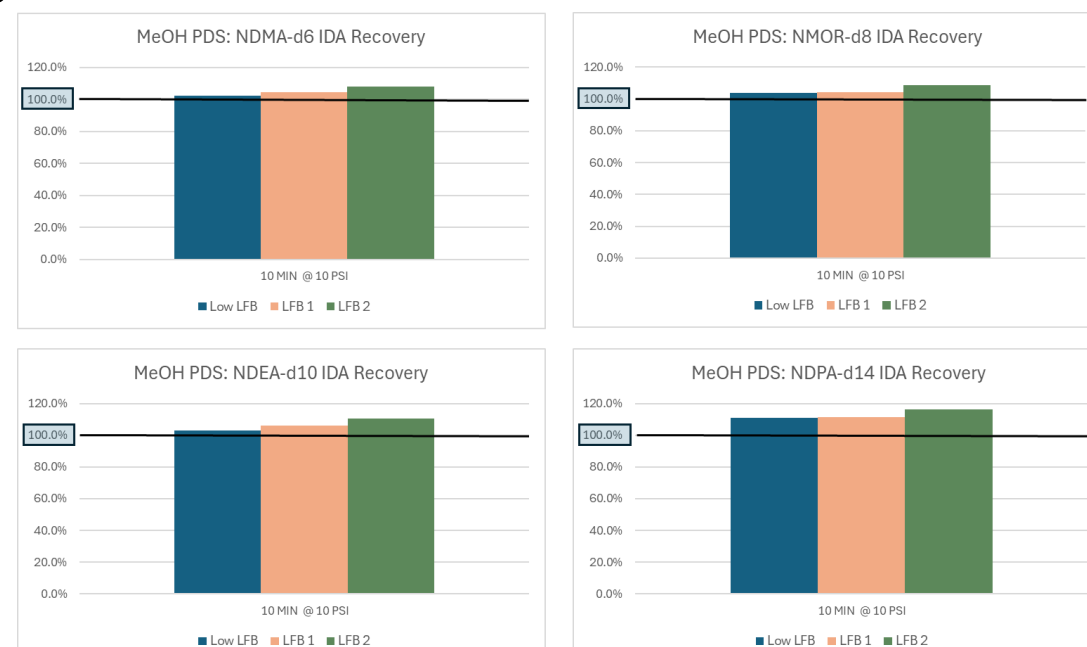
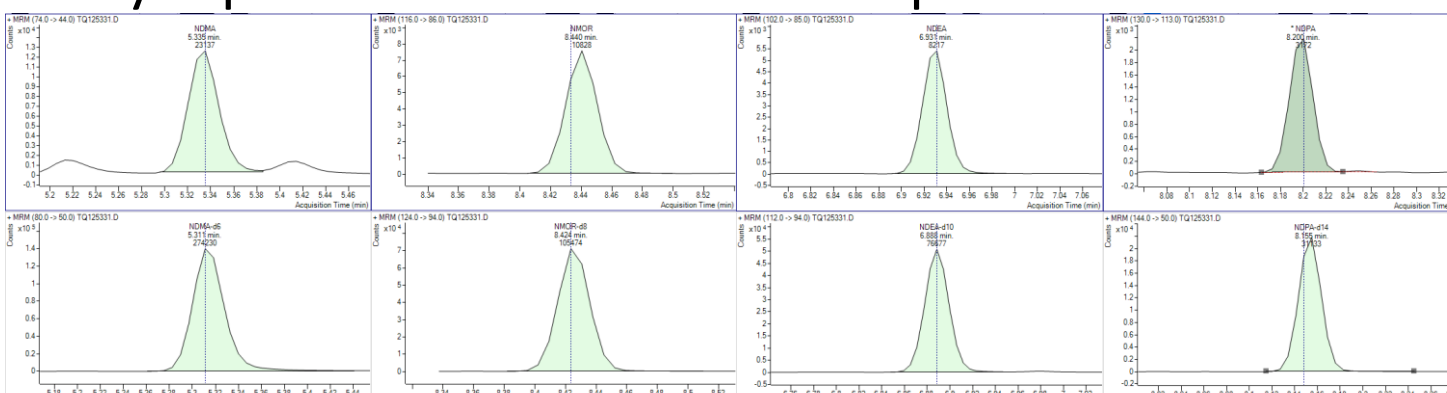


Figure 5d. MeOH PDS: Calibration Curve IDA Response Recovery

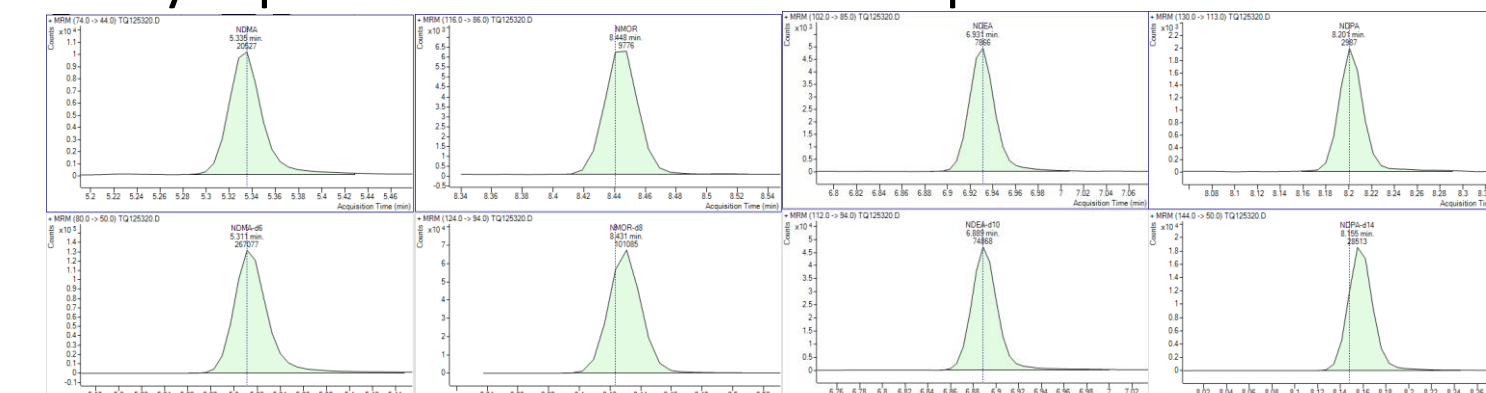
Calibration Levels	NDMA-d <sub>6</sub> (Area Count)	NMOR-d <sub>8</sub> (Area Count)	NDEA-d <sub>10</sub> (Area Count)	NDPA-d <sub>14</sub> (Area Count)
CAL A (2 ng/L)	267077	101085	74868	28513
CAL B (5 ng/L)	266059	101063	74604	28262
CAL C (10 ng/L)	268624	101947	74619	27658
CAL D (25 ng/L)	266742	100700	74021	27896
CAL E (50 ng/L)	263562	102078	73813	27580
CAL F (100 ng/L)	277554	103563	75481	28390
<b>ICAL Average:</b>	<b>268270</b>	<b>101739</b>	<b>74568</b>	<b>28050</b>

Figure 6. Analyte (2 ng/L) and IDA (25 ng/L) peak chromatograms for both extracted sample & direct made calibration standard, using MeOH PDS.

A. MeOH PDS: Extracted peak chromatograms. Top are Analyte peaks and bottom are IDA peaks.



B. MeOH PDS: Direct spike peak chromatograms. Top are Analyte peaks and bottom are IDA peaks.



## Results and Discussion III

Recovery results between EPA 521 and the in-house concentration settings were comparable (Figure 7a & 7b). Equivalent recovery was observed at the higher setting of 45°C with a nitrogen flow rate of 3.5 L/min.

Figure 7a & 7b. Comparing EPA 521 and OCWD extract concentration settings. Figure 7a presents IDA % recovery and Figure 7b presents Analyte % recovery.

Figure 7a. Concentration Settings and IDA % recovery

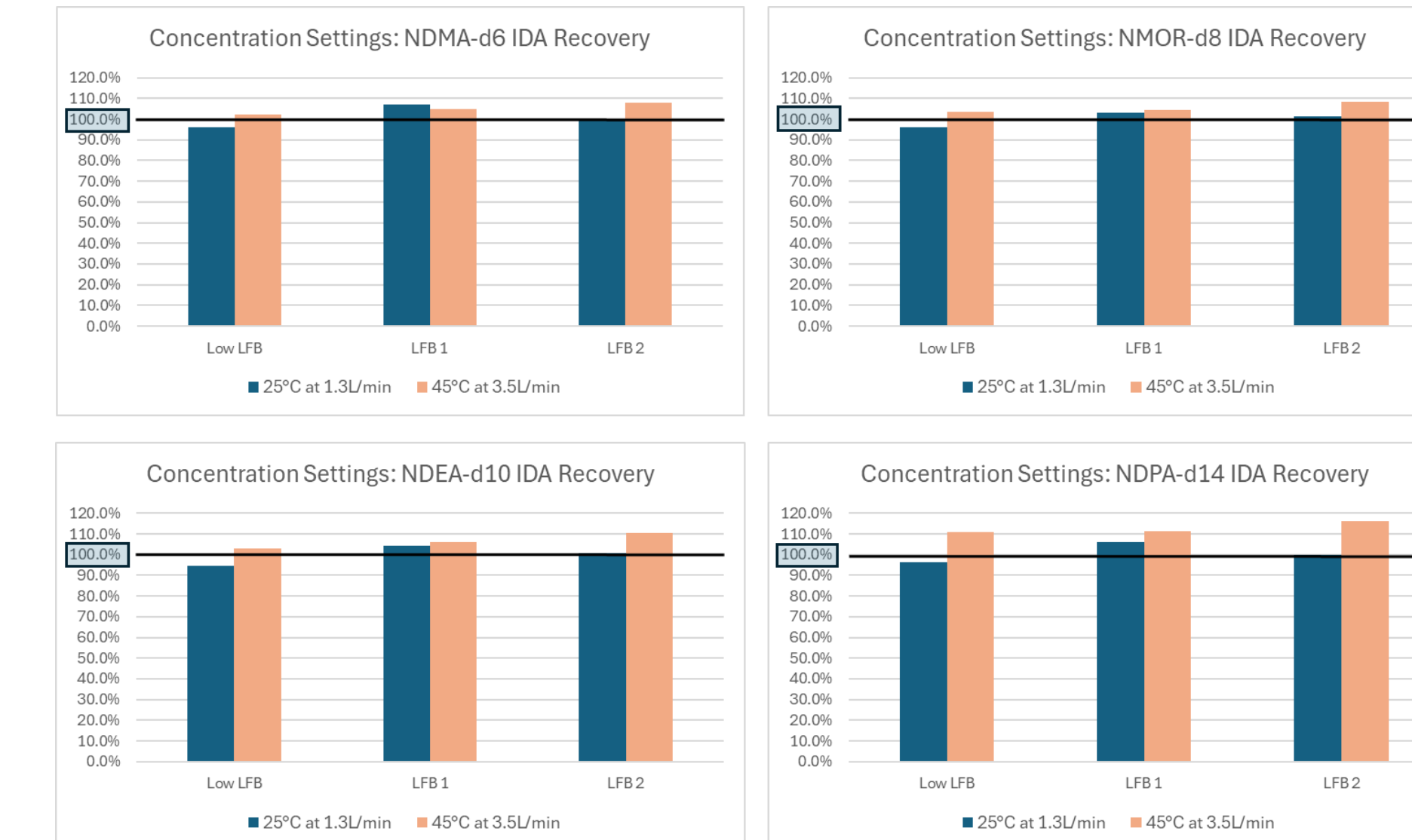
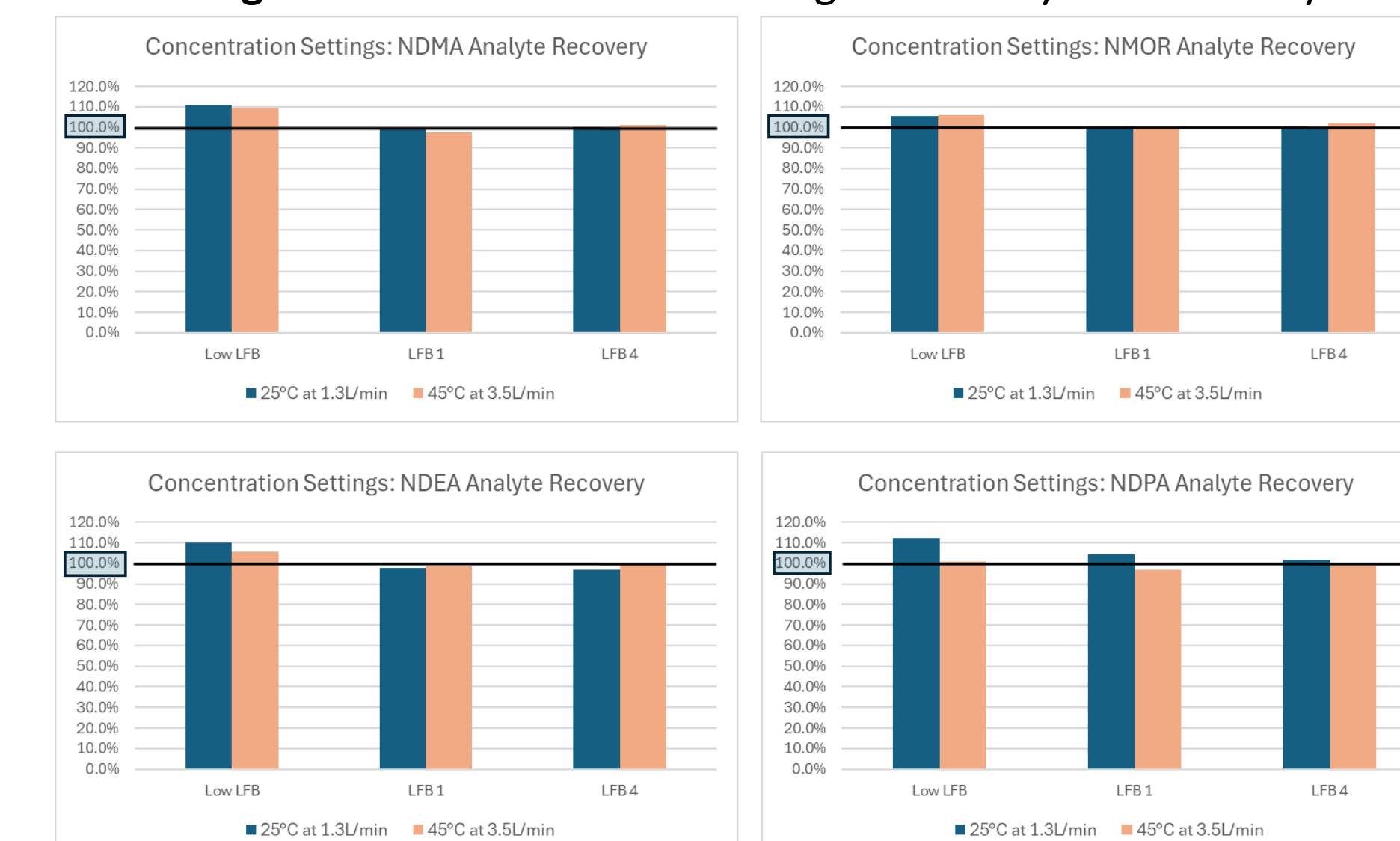


Figure 7b. Concentration Settings and Analyte % recovery



## Conclusions

- The dry time and PSI setting of the AutoTrace system influences IDA recoveries. Optimal recovery for all 4 IDA compounds was observed at a dry time of 10 minutes with a pressure setting of 10-15 PSI.
- Using MeOH PDS for calibration standard preparation and sample extraction upholds accurate recovery. This allows to use a single PDS for both direct calibration standard preparation and sample extraction, reducing preparation time.
- Recovery was not compromised when the concentrator's settings were increased to 45°C with a nitrogen flow rate of 3.5 L/min. The increased concentrator settings reduced the concentration time from 30 minutes to 10 minutes when using a TurboVap II.

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