Large Volume ASPEC® 274: Determination of Nitrosamines in Drinking Water

TECHNICAL NOTE TN212

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INTRODUCTION

Nitrosamines are a class of semi-volatile organic chemical compounds characterized by a nitroso group attached to an amine group. Examples of nitrosamine structures are shown in Figure 1.

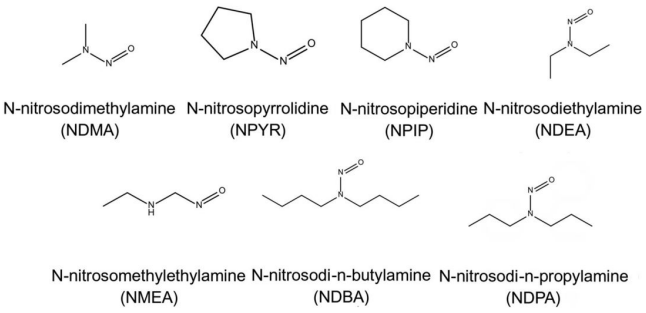

Figure 1
Example of N-Nitrosamines chemical structure

As of 2011, N-nitrosodimethylamine (NDMA) was the primary nitrosamine identified in samples from U.S. municipal water systems. Contamination with NDMA is a concern because NDMA is highly miscible with water and the US Environmental Protection Agency (EPA) has classified it as a B2 (probable human) carcinogen. NDMA may be formed as a byproduct at water treatment plants that utilize chloramines as disinfectants as well as in industrial environments such as tanneries, fish processing facilities, foundries, and manufacturing plants that produce rubber, tires, pesticides, surfactants, amines, and dyes.[1]

The US EPA has established Method 521 for determination of nitrosamines in drinking water.[2] This method uses solid phase extraction (SPE) and capillary column gas chromatography (GC) with large-volume injection and chemical ionization tandem mass spectroscopy (MS) (EPA 2005). The screening level for NDMA in tap water was calculated as 0.11 ng/L for NDMA. Another study reported a method that is a combination of SPE and LC/MS/MS for determination of NDMA in surface water, groundwater, and wastewater samples with a quantification limit of 2 ng/L.[3] In this tech note we describe a method for automating US EPA Method 521 using the Gilson ASPEC® 274 Large Volume System (Figure 2).

Figure 2
ASPEC® 274 Large Volume System shown with the system organizer

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MATERIALS AND METHODS

Analytes and a surrogate analyte are extracted by passing a 0.5 L water sample through a 6 mL SPE cartridge containing 2 g of 80-120 mesh coconut charcoal. The organic compounds are eluted from the solid phase with a small volume of methylene chloride (12 mL). To remove any traces of water, the methylene chloride extract is dried and concentrated on a 6 mL anhydrous sodium sulfate SPE cartridge, then the extract is concentrated to approximately 0.9 mL, and then an internal standard is added.

The sample components are separated, identified, and measured by injecting an aliquot of the concentrated extract onto the fused silica capillary column of a GC/MS/MS system equipped with a large volume injector (LVI), and operated in the chemical ionization (CI) mode.

SYSTEM DESCRIPTION

The ASPEC large volume solution is built on the ASPEC® 274 equipped with four valve selectors (VALVEMATE® II Valve Actuator) as shown in Figure 3.

The valves allow the selection of external bottles containing large volume samples that are loaded onto the SPE cartridges via the ASPEC® 4260 Dual Syringe Pump equipped with 10 mL syringes. Each VALVEMATE is equipped with a 10-port, low pressure valve and each central port is connected to a dedicated probe (Figure 3). The first position is connected to water used during the SPE conditioning steps and as a rinsing solution between samples. To improve rinsing and remove any traces of water, the tenth position is connected to a methylene chloride bottle. The other eight ports are available for samples. This system is able to prepare up to 32 samples by batches of four samples in parallel.

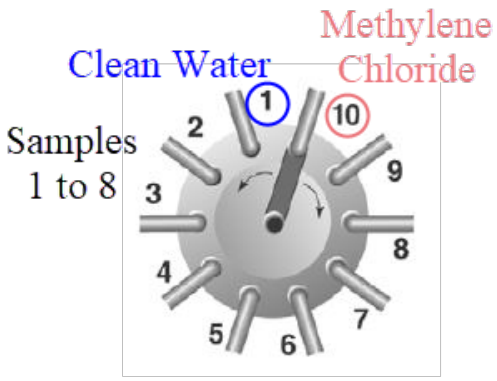

Figure 3
VALVEMATE® II VALVE ACTUATOR, 10-port, low pressure valve

SPE PROCEDURE

Manual Protocol

The manual protocol described in EPA Method 521 is outlined in Table 1.

Table 1
EPA Method 521

EXTRACTION #1	COCONUT CHARCOAL CARTRIDGE
Charging Desk Stand	Fill the cartridge with approximately 3 mL methylene chloride. Repeat once.
	Fill the cartridge with approximately 3 mL methanol. Repeat once.
	Fill the cartridge with approximately 3 mL methanol and elute to just above the top frit — not allowing the cartridge to go dry at the end. From this point forward, do not allow the cartridge to go dry.
Sample Loading	Load 500 mL of water at an approximate flow rate of 10 mL/min.
	After all of the sample has passed through, dry the cartridge for ten minutes.
Elution	Fill each cartridge with methylene chloride. Allow the sorbent to soak in methylene chloride for approximately one minute.
	Continue to add methylene chloride to the cartridge as it is being drawn through in a dropwise fashion until the volume of extract is about 12 or 13 mL.
EXTRACTION #2	**ANHYDROUS SODIUM SULFATE CARTRIDGE**
Conditioning	Pre-wetted with a small volume of methylene chloride prior to passing the extract through.
Sample Load and Collect	Pass the charcoal cartridge eluted fraction and collect the dried extract (12–13 mL) in a clean centrifuge tube.
Wash and Collect	Wash the sodium sulfate sorbent with at least 3 mL methylene chloride and collect the solvent in the same tube as the extract.

Automated Protocol on TRILUTION® LH SOFTWARE

All manual steps are easily automated and both extractions happen sequentially, the first extract being automatically loaded on to the drying cartridge. The steps in the automated protocol are shown in Figure 4.

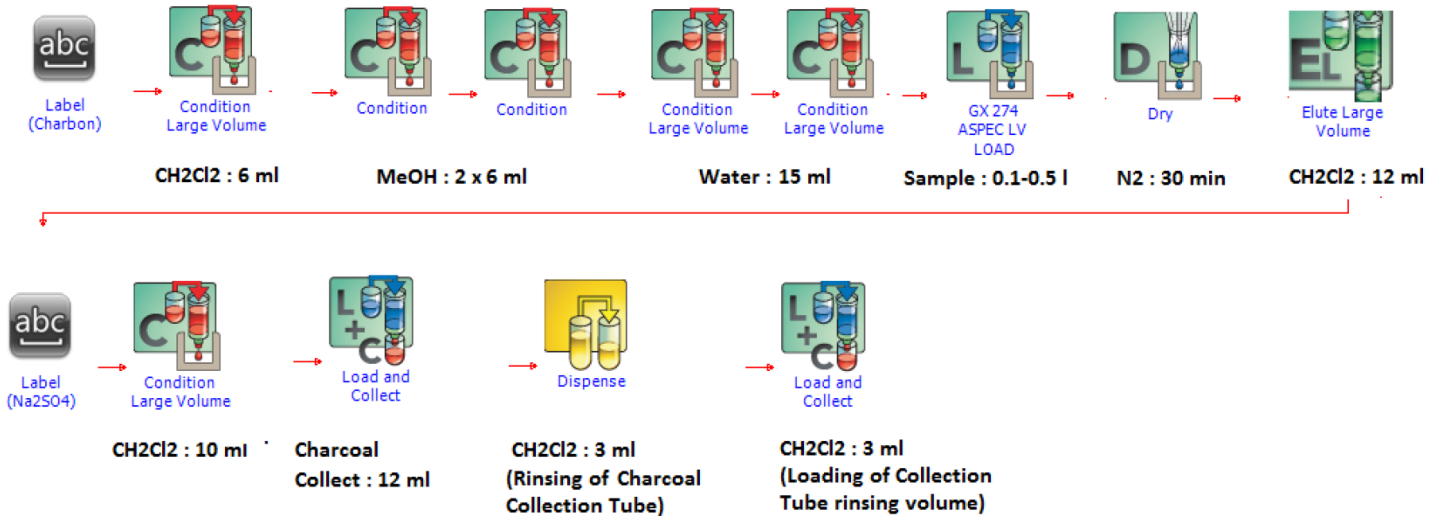

Figure 4
Schematic of TRILUTION® LH Software method

PRECAUTIONS

Reagents and SPE consumables should be considered a potential source of NDMA contamination. Therefore, EPA Method 521 recommends analyzing reagent blanks, including SPE cartridges, to avoid false positives and ensure that presence of a contaminant in reagents or consumables will not prevent the identification and quantitation of NDMA in the samples. Rubber and latex products may contain trace levels of NDMA and should be avoided when running Method 521. Additionally, it should be noted that another potential source of contamination is the repeated injection from autosampler vials that have Teflon® [PTFE, polutetrafluoroethylene] coated rubber septa as this could result in the unintended introduction of method analytes into samples.[2]

The ASPEC 274 bed layout employed with this method features glass bottles for solvents and two sets of SPE racks for 16 x 6 mL cartridges and 16 x 100 mm glass collection tubes as shown in Figure 5.

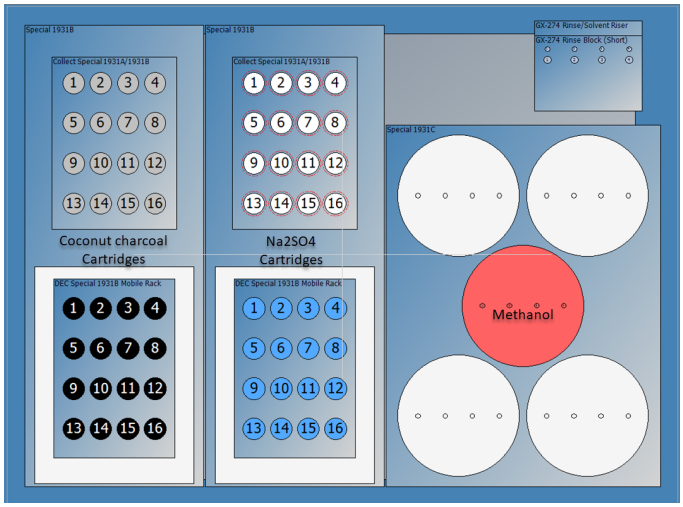

Figure 5
Schematic of bed layout on ASPEC® 274

TRILUTION LH FEATURED TASKS

This application highlights the flexibility of the powerful TRILUTION LH software with the use of specific tasks to improve results and usability.

Ability to Load Large Sample Volumes

When volumes exceed 100 mL, sample bottles are usually placed outside of the ASPEC 274 and are loaded on the SPE cartridges using a selection valve (VALVEMATE). It is critical to minimize cross contamination risks by applying dedicated rinsing. The specific TRILUTION LH task “GX-274 ASPEC LV Load” allows for automatic valve port selection, precise loading volume (taking account for dead volume) and an additional rinsing step with a second solvent in which the NDMA is highly soluble to remove any traces in the tubing (Figure 6).

Figure 6
TRILUTION® LH Software specific tasks

Ability to Use Large Solvent Volumes

To improve speed and rinsing between samples, two solvents (water and methylene chloride) are located outside of the liquid handler tray and directly connected to the VALVEMATE. A specific task allows for easy selection of the correct channel (FIgure 7).

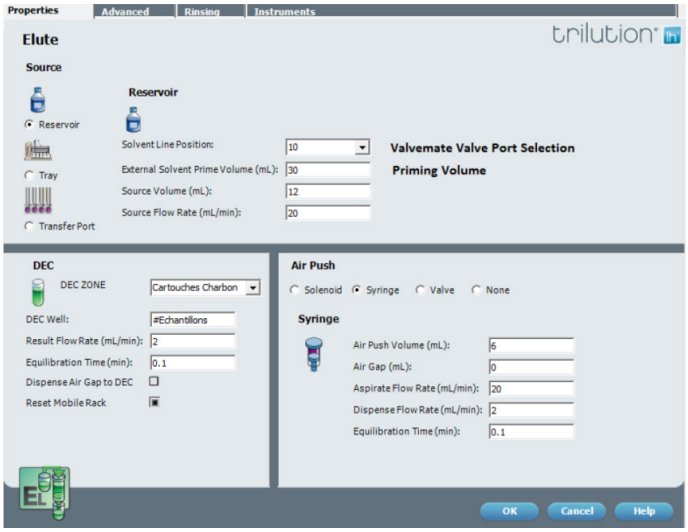

Figure 7
TRILUTION® LH Software Large Volume task

To fully automate the method and avoid any risk of contamination, which is particularly important when extracting traces of contaminants, TRILUTION LH includes automatic rinsing and purging steps at the beginning and at the end of the users’ run (Figure 8).

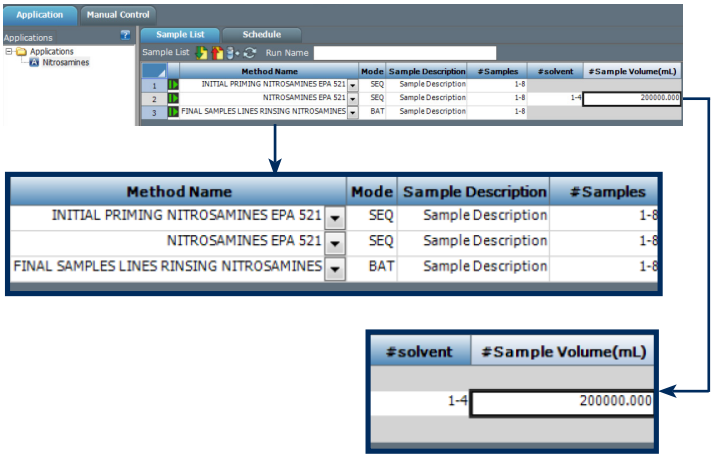

Figure 8
TRILUTION® LH Software automatic rinsing and purging steps

CONCLUSION

The EPA Method 521 "Determination of nitrosamines in drinking water by solid phase extraction and capillary column gas chromatography with large volume injection and chemical ionization tandem mass spectrometry" can be fully automated on the ASPEC 274 with important benefits:

- High extraction reproducibility with precise volume management and positive pressure elution
- High throughput with four extractions run in parallel
- Up to 32 samples can be treated without user intervention (16 with segregated waste)
- Capability to load large volumes (500 mL) and smaller volumes (12 mL) on the same protocol
- Dual extractions done sequentially
- Minimal risks of cross contamination
- Possibility to segregate waste between aqueous and organic solvents

REFERENCES

[1] United States Environmental Protection Agency, Technical Fact Sheet – N-Nitroso-dimethylamine (NDMA), EPA 505-F-17-005, (2017) https://www.epa.gov/sites/production/files/2017-10/documents/ndma_fact_sheet_update_9-15-17_508.pdf

[2] Munch, J W. METHOD 521: Determination of nitrosamines in drinking water by solid phase extraction and capillary column gas chromatography with large volume injection and chemical ionization tandem mass spectrometry (MS/MS). U.S. Environmental Protection Agency, Washington, DC. (2005) https://cfpub.epa.gov/si/si_public_record_report.cfm?dirEntryId=103912&simpleSearch=1&searchAll=521

[3] Topuz, E., Aydin, E. & Pehlivanoglu-Mantas, E. Water Air Soil Pollut (2012) 223: 5793. https://doi.org/10.1007/s11270-012-1315-1

TRADEMARKS

NOTICE

ORDERING INFORMATION

Table 2
List of items for automation of method EPA 521

PART NUMBER	DESCRIPTION	QUANTITY
2614010	ASPEC 274,TWO DUAL 4260, W/Z-DRIVE	1
26046233	INERT GUIDE FOOT, 2.3 MM, ASPEC 274	1
SPL-1931F-HDW	LOCATOR, 274/271 WATER ANALYSIS	1
25025345	SYRINGE, 10ML	4
26047035	KIT, ASPEC LARGE VOLUME,FEP,PLUMBING	4
27067374	PROBE,221x1.5x1.1MM CON BEV .45ID TIP	8
26044016	ASY, 27X RINSE-SOLVENT DELIVERY,178MM	1
331052AB	VALVEMATE II,GSIOC,GILSON	4
49400006	VALVE,PREP,MULTI-POS,10-PORT,0,060,PPS	4
4701438630	TUBING,VITON,0.313 X 0.438,20FT	1
470343706	TUBING,TYGON,0.313 X 0.438	20
2644707	KIT,ASPEC 274 AIR/GAS PLUMBING	1
SPL-1931H-HDW	PRESSURE REGULATOR ASSEMBLY FOR SPL-1931	1
2604706	ASY, 27X SHIELD	1
21050000	27X SYSTEM ORGANIZER	1
SPL-1931E-HDW	BRKT,SYSTEM ORGANIZER VALVEMATE II	4
SPL-1931L-SFW	TASKS,TLH 4 RACK FILES SPL-1931	1
SPL-1931B-HDW	RACK, 274 LVSPE 6mL 16-16x100 TUBES	2
2954730	CAP,6ML COLUMN,NATURAL PE (1000/PK)	1
SPL-1931C-HDW	RACK, 274 5-650mL GLASS BOTTLE W/O BTL	1
54370601	BOTTLE,SOLVENT,650ML 4/PK	1
54350001	TUBES,16 X 100MM,15ML,GLASS (250/PK)	1
361832	508 INTERFACE MODULE 110-220V	1
21063024	TRILUTION LH 4.0 LICENSE, LIFETIME	1