Water Quality Growth and Change, Advanced Technology Method Change to Prescribe a Desirable Future to US EPA Method 521, (2004)

Konjit Tadigo [1]; Andrew Eaton [1]; Charles Grady [1]; Ron Honnold* [2]
[1] Eurofins Eaton Analytical Inc, Monrovia, California; [2] Agilent Technologies Inc, Prescott, Arizona

ASMS 2016
WP 191

Introduction

The goal of this project is to show validation by a direct comparison of an Electron Ionization (EI) Tandem Quadrupole (TQ) method and the currently used Internal Chemical Ionization (CI) Ion Trap quadrupole method with split sample sets. Over time, Ion Trap MS systems have become more and more rare, leaving one to wonder about the future of the analysis of *N*-Nitrosamines by US EPA Method 521, (2004). The US EPA has indicated a new Mass Spectrometer (MS) platform may be used (Section 6.11.3 of the method states: "The tandem mass spectrometer may be either a triple quadrupole or an ion trap"), but the sample preparation and sensitivity criteria must follow US EPA Method 521 guidelines. Tandem mass spectrometry (TQ) using electron ionization (EI) now yields low parts per trillion detection limits that satisfy the requirements for detection of these compounds in aqueous matrices.

Impetus for the Project

EPA Method 521 was written around a now obsolete technology (Varian/Agilent Ion Trap).

EPA could regulate nitrosamines.

N-Nitrosamines have been identified as drinking water or wastewater contaminants and are a health and regulatory concern.

There is a need for an alternative rugged method.

Approach to the Project

Eurofins Eaton Analytical (EEA) Monrovia performs US EPA 521 extractions and analysis routinely (>2500/year).

We evaluate the sensitivity and speed of a Gas Chromatograph Tandem Mass Spectrometer (GC-TQ) for the measurement of EPA 521 as alternative.

EEA Monrovia also extracts samples for the Lowest Concentration Minimum Reporting Level (LCMRL), Detection Level (DL), Critical Level (CL) determination by both Varian 4000 Ion Trap and by Agilent 7010 GC-TQ, and examples will be shown.

A method to show the advancements in instrumentation and sensitivity to achieve detection limits compared to those currently being used is demonstrated.

An analytical procedure was developed on the Agilent 7890B GC / 7010 GC-TQ in electron ionization mode (EI) using the Varian 4000 Ion Trap chemical ionization mode (CI) method.

The gas chromatographs (GC) were configured with similar temperature programmable inlets, 30 meter column (DB-1701MS), and automatic liquid sampling systems (ALS).

The new analysis time was less than 15 minutes vs the current approximately 30 minute analysis time.

Validation was done comparing the Varian 4000 CI Ion Trap system and the Agilent 7010 EI Tandem quadrupole system.

The EI Tandem Quadrupole method uses 1.0 uL^{-1} injection vs the current need of from 10.0 to 50.0 uL^{-1} injection volume on the Ion Trap system.

Experimental

Table 1. List of *N*-Nitrosamine analytes

Compound Name	Abbreviation	Retention Time	
N-nitrosodimethylamine	NDMA-d6	5.95	Surrogate
N-nitrosodimethylamine	NDMA	5.99	Target
N-nitrosomethyethylamine	NMEA	7.54	Target
N-nitrosodiethylamine	NDEA	8.75	Target
N-nitrosodipropylamine	NDPA-14	11.60	Internal Std
N-nitrosodipropylamine	NDPA	11.64	Target
N-nitrosomorpholine	NMOR	12.18	Target
N-nitrosopyrrolidine	NPYR	12.48	Target
N-nitrosopiperdine	NPIP	12.83	Target
N-nitrosodi-n-butylamine	NDBA	14.48	Target
N-nitrosodi-n-phenylamine	NDPhA	21.26	Target

New GC and MS Conditions:		
Column	DB-1701ms, 30 m, 0.25 mm ID, 1.0 µm film thickness	
Injection volume	1.0 µL^{-1}	2mm Dimpled, UI Liner
Splitless injection	Purge flow to split vent	100 mL min^{-1} at 0.8 min
MMI inlet temperature	35 °C for 0.1 min, 600 °C min^{-1} to 260 °C	
Oven temperature program	33 °C for 1 min	
	35 °C min^{-1} to 80 °C, for 2 min.	
	10 °C min^{-1} to 140 °C, for 0 min 50 °C min^{-1} to 250 °C for 2.0 min	
Carrier gas	Helium at 1.2 mL min^{-1} constant flow	
Transfer line temperature	280 °C	
MS parameters used in the method:		
Ionization mode	EI; using HES ion source	
Source temperature	280°C	
Quadrupole temperatures	150°C	
Collision gas Quench gas	1.5 mL min^{-1} 4.0 mL min^{-1}	
Emission	100µA	

Compound	Transition	CE	Compound	Transition	CE
NDMA-d6	80>50.1	6	NMOR	116>56.1	20
NDMA-d6	80>48.1	14	NMOR	116>86	4
NDMA	74>42.1	14	NPYR	100>70	10
NDMA	74>44.1	6	NPYR	100>55	10
NMEA	88>71	6	NPIP	114>97	10
NMEA	88>43	10	NPIP	114>84	10
NDEA	102>56.1	12	NDBA	116>99	20
NDEA	102>85	5	NDBA	158>141.1	6
NDPA-d14	144>126.1	5	NDPhA	169>77	20
NDPA-d14	144>50.1	10	NDPhA	169>66	20
NDPA	130>43	8			
NDPA	101>70	20			

Results and Discussion

Table 2: LCMRL by GC-TQ

Compound	LCMRL	DL	Critical Level
NDMA	0.52	0.25	0.17
NMEA	0.39	0.16	0.09
NDEA	0.32	0.13	0.09
NDPA	1.20	0.58	0.36
NMOR	0.75	0.27	0.14
NPYR	1.10	0.36	0.13
NPIP	0.59	0.29	0.16
NDBA	0.99	0.51	0.31

Table 3: LCMRL by Ion Trap

Detection Limit (DL) was calculated from extracted replicates

Compound	LCMRL	DL	Critical Level
NDMA	6.7	0.19	0.21
NMEA	2.2	0.48	0.31
NDEA	6.9	0.74	0.48
NDPA	5.6	0.5	0.5
NMOR	TBD	.41	0.35
NPYR	TBD	.43	0.44
NPIP	1.9	0.38	0.39
NDBA	2	0.42	0.35

Figure 1: TQ Calibration Has a Wide Range
0.5 to 100 ppt for results in *Table 2* (above) and *Figures 2-5*

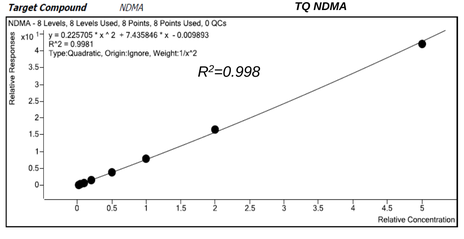


Figure 2: Real Extract Sample Comparison- 0.5 to 3 ppt NMEA

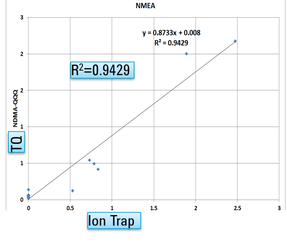


Figure 3: Real Extract Sample Comparison- 0.5 to 10 ppt NDMA

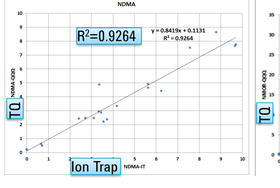


Figure 4: Real Extract Sample Comparison- 0.5 to 35 ppt NMOR

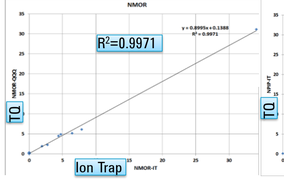
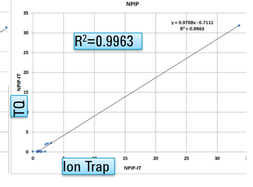


Figure 5: Real Extract Sample Comparison- 0.5 to 35 ppt NPIP



Results and Discussion

Figure 6 : Calibration comparison TQ to IT, 2.0 to 100 ppt for extracted sample sets (*Table 4)*

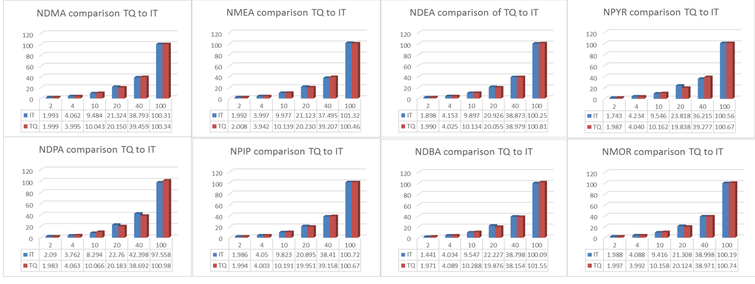


Table 4: Split Extracted Real Samples for comparison between the Tandem Quadrupole and Ion Trap Instruments

Sample Name	NDMA TQ	NDMA IT	NMEA TQ	NMEA IT	NDEA TQ	NDEA IT	NDPA TQ	NDPA IT	NPYR TQ	NPYR IT	NMOR TQ	NMOR IT	NPIP TQ	NPIP IT	NDBA TQ	NDBA IT
MBLK	0.00	0.00	0.00	0.48	0.00	0.00	1.42	0.00	0.00	0.00	0.00	0.00	0.00	0.82	0.64	0.49
CCCL 2PPT	2.26	2.04	2.21	2.03	2.14	1.94	2.08	2.55	2.01	1.97	2.01	1.99	2.01	1.70	1.80	
67	0.96	0.51	0.00	0.00	0.00	0.00	0.96	0.00	0.00	0.00	1.04	1.38	0.00	0.00	1.83	1.34
68	1.17	0.80	0.00	0.00	0.00	0.14	0.00	0.00	0.00	0.00	0.00	0.71	0.00	0.45	1.10	0.64
81	0.00	0.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.31	0.00	0.71	0.00	0.48	0.00	0.33
82	0.65	0.85	0.00	0.00	0.00	0.18	1.39	0.00	0.00	0.00	0.00	0.39	1.00	0.00	0.43	0.97	1.58
83	1.49	1.01	0.00	0.00	0.00	0.11	0.52	0.00	0.00	0.00	0.00	0.79	0.00	0.44	1.04	0.00
98	1.28	1.23	0.00	0.47	0.00	0.17	0.49	0.00	0.00	0.00	0.00	0.44	0.62	0.00	0.54	0.99	0.40
73	163.53	157.96	0.00	0.55	0.00	0.16	0.45	0.00	0.00	0.78	2.28	2.50	0.00	0.43	0.45	0.53
74	36.15	33.46	0.00	0.46	0.00	0.36	0.39	0.00	0.00	0.59	0.72	0.47	0.00	0.93	1.27	0.77
75	151.00	149.23	0.00	0.49	0.00	0.00	1.95	0.00	0.00	0.63	2.46	2.62	0.00	0.45	0.68	0.41
76	7.84	6.78	0.00	0.00	0.00	0.00	0.57	0.00	0.00	0.30	0.93	0.45	0.00	1.92	2.20	1.45
77	139.84	135.64	0.00	0.48	0.00	0.10	1.83	0.00	0.00	0.82	2.40	2.75	0.00	0.45	0.49	0.56
78	7.01	6.94	0.00	0.00	0.00	0.18	1.48	0.00	0.00	0.68	0.53	1.44	0.00	0.80	1.14	1.12
79	140.05	136.69	0.00	0.50	0.00	0.18	2.13	0.00	0.00	0.65	2.99	3.03	0.00	0.55	0.45	0.44
781	132.18	133.22	0.00	0.00	0.00	0.37	0.43	0.00	0.00	0.73	2.69	3.67	0.00	0.00	0.65	0.61
782	2.53	1.88	0.00	0.00	0.00	0.00	1.84	0.00	0.00	0.51	1.13	0.00	0.00	0.77	1.36	1.27
783	128.14	108.21	0.00	0.46	0.00	0.36	1.67	0.00	0.00	0.00	2.67	2.82	0.00	0.00	0.65	0.66
784	1.25	0.77	0.00	0.00	0.00	0.50	0.33	0.00	0.00	0.56	0.41	1.20	0.00	0.71	0.90	1.46
14	0.49	0.00	0.00	0.00	0.00	0.54	1.76	0.00	0.00	0.00	2.76	3.14	0.00	0.00	0.76	0.76
CCCM 40PPT	43.05	41.32	41.25	37.44	39.85	39.95	39.37	42.19	38.59	39.35	38.68	40.20	39.46	42.77	40.26	38.46
CCC 100PPT	108.98	102.51	106.60	103.26	104.39	117.47	101.58	92.81	99.15	102.49	97.84	106.73	101.05	105.86	103.19	108.86
LCS3	87.88	71.51	89.65	73.44	85.77	85.09	86.53	75.48	86.65	76.02	89.31	73.52	91.12	83.06	90.44	87.47

Notes: 1) TQ results ***only*** subject to 0.3 ppt reporting limit 2) IT results for NDPA all found to have incorrect RT; reported as zero

Conclusions

The 7010-TQ has a run time of 15 minutes with excellent separation of all compounds without NDPhA where the Ion Trap MS run time is close to 30 minutes without NDPhA.

The 7010-TQ is consistently more sensitive, up to 10x running in EI-MS/MS mode than the Ion Trap running in CI-MS/MS mode.

Comparison of data from the Ion Trap with the Tandem Quadrupole shows excellent correlation.

The ability to use less sample, 0.5-1.0 uL^{-1} vs the current 8.0-10.0 uL^{-1} required by the Ion Trap technology.

Next step is to run more split extracted samples with other labs and create a SOP/Method.