Method 521

Using

7010 GC/MS Triple Quad

Introduction

- The purpose of this project was to validate and show the performance of 7010 GC/MS Triple Quad for Method 521 with comparison to the Ion Trap(EPA approved instrument for Method 521) without deviating from EPA guidelines for sample preparation.

- EPA OGWDW considers alternate detection techniques without changing sample preparation.

The Importance of This Project

- Right now method 521 is performed on 2000/4000 Varian/ion trap instruments which are going to be phased out.
- Due to the concern of N-Nitrosamines occurrence in drinking water and waste water, EPA might regulate these compounds.
- Better technology – low parts per trillion detection limits in aqueous matrices

How The Experiment Was Done:

- Eurofins Eaton Analytical extracts and analyzes >3000 samples per year for method 521.
- Similar analytical procedures used as the ion trap to develop the method on the TQ.
- GC programs were very similar,
- Same inlet temperature
- 30 meter DB 1701 MS column was used for TQ Vs. VF-5ms
- Injection volume: 10ul for ion trap Vs. 1ul for TQ

GC and MS Parameters: Table 1

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	

Compounds With Transitions And Their Collision Energy: Table 2

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				

Retention Times: Table 3

Compound Names	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

Low level Detection Information

- Lowest concentration minimum reporting level(LCMRL), Detection level(DL), and critical level(CL) was conducted to determine the sensitivity of the instrument
- Used the same extracts for TQ and ion trap

LCMRL Comparisons

Table 4: 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

GC-TQ is almost an order of magnitude more sensitive than the ion trap

Table 5: LCMRL by Ion Trap

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

Target Compound *NDMA*

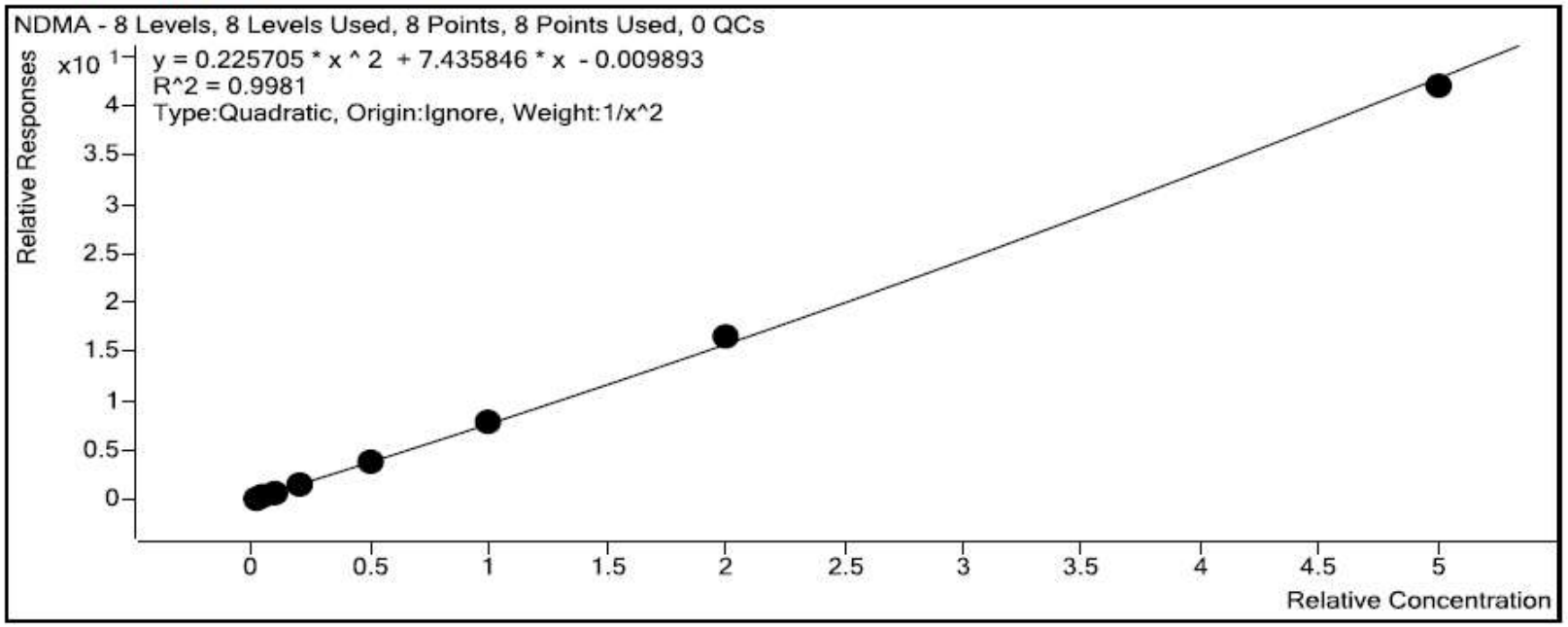


Figure 2: Real Extract Sample Comparison- 0.5 to 3 ppt NMEA

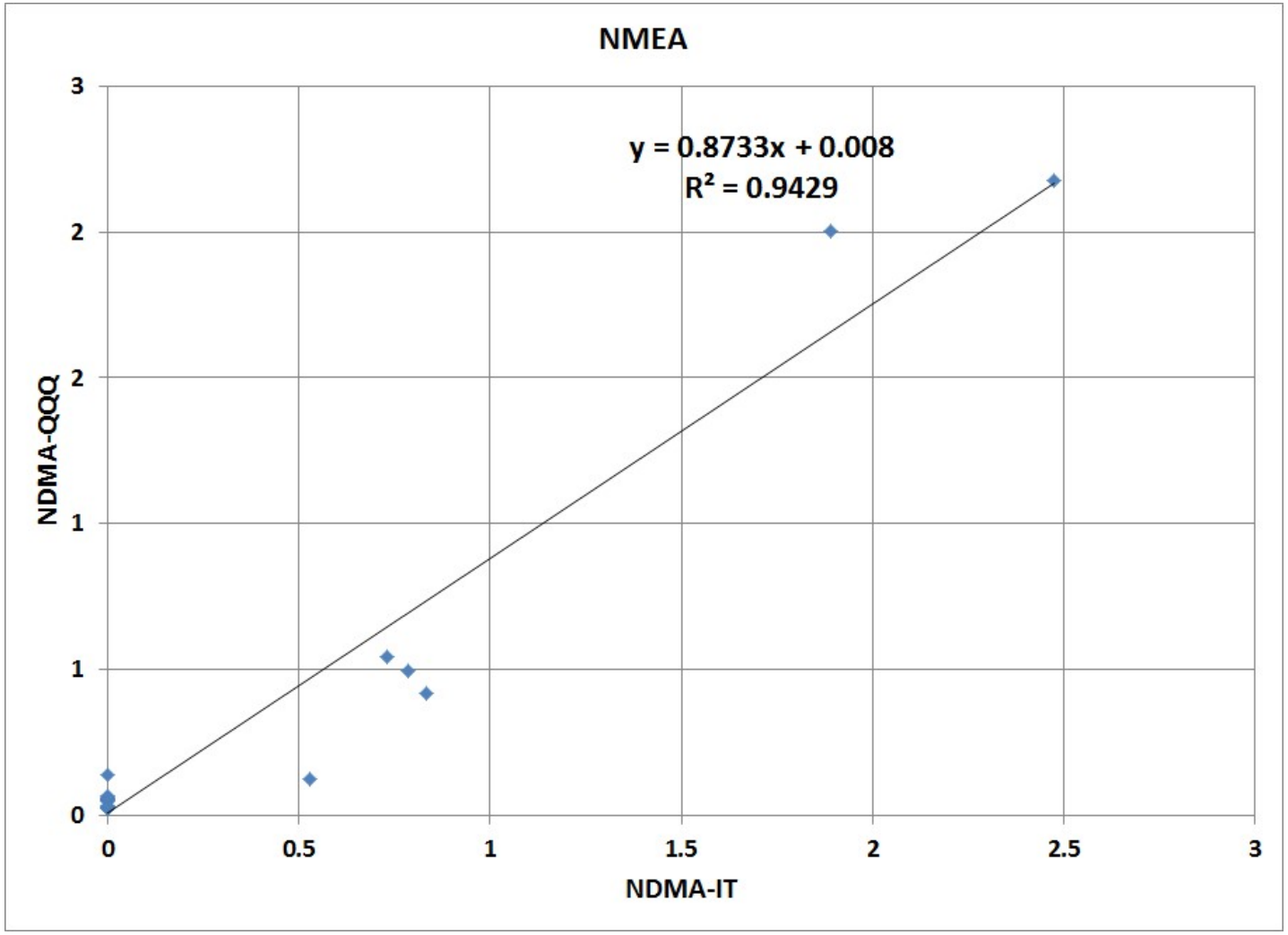


Figure 3: Real Extract Sample Comparison- 0.5 to 10 ppt NDMA

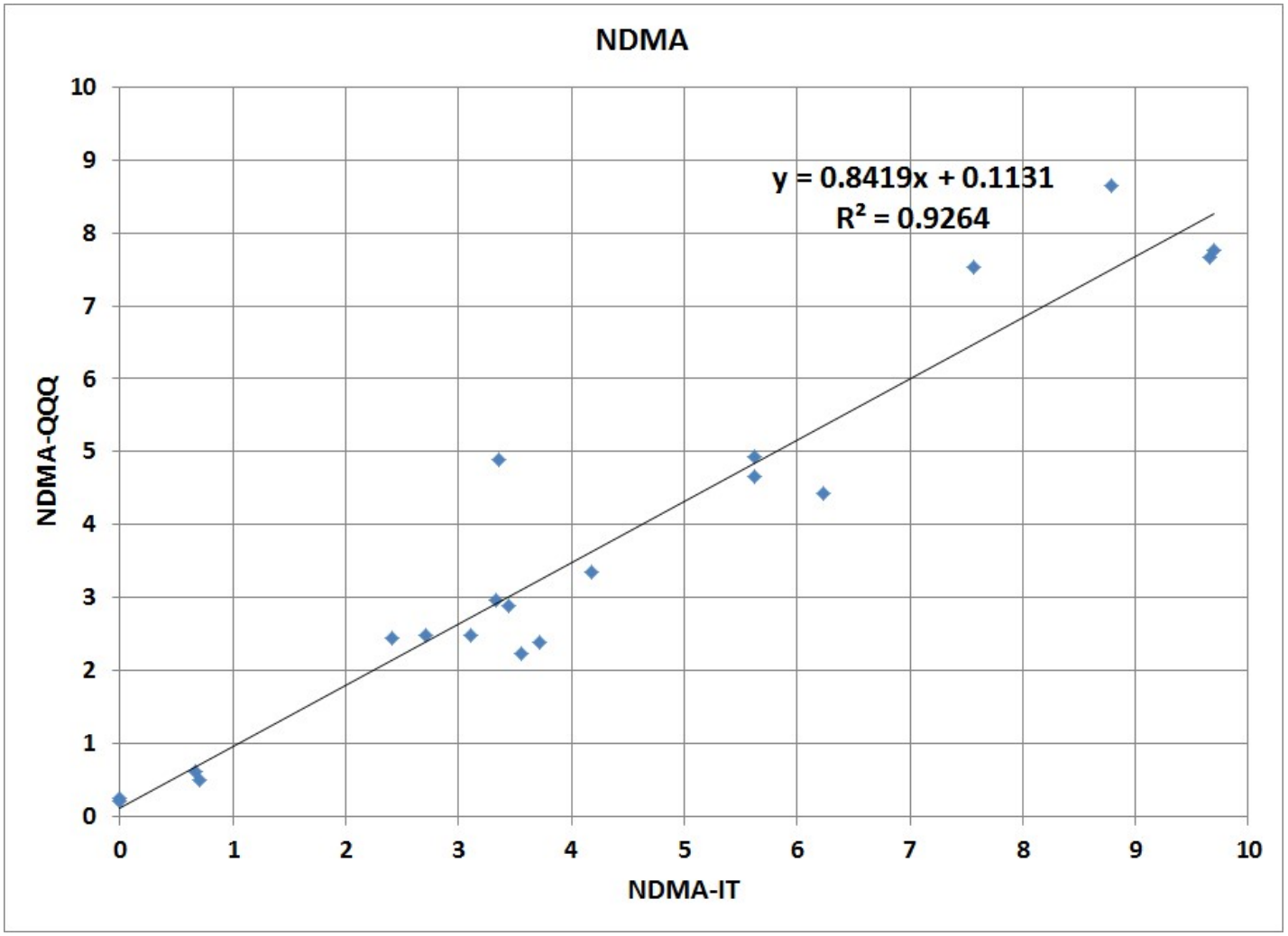


Figure 4: Real Extract Sample Comparison- 0.5 to 35 ppt NMOR

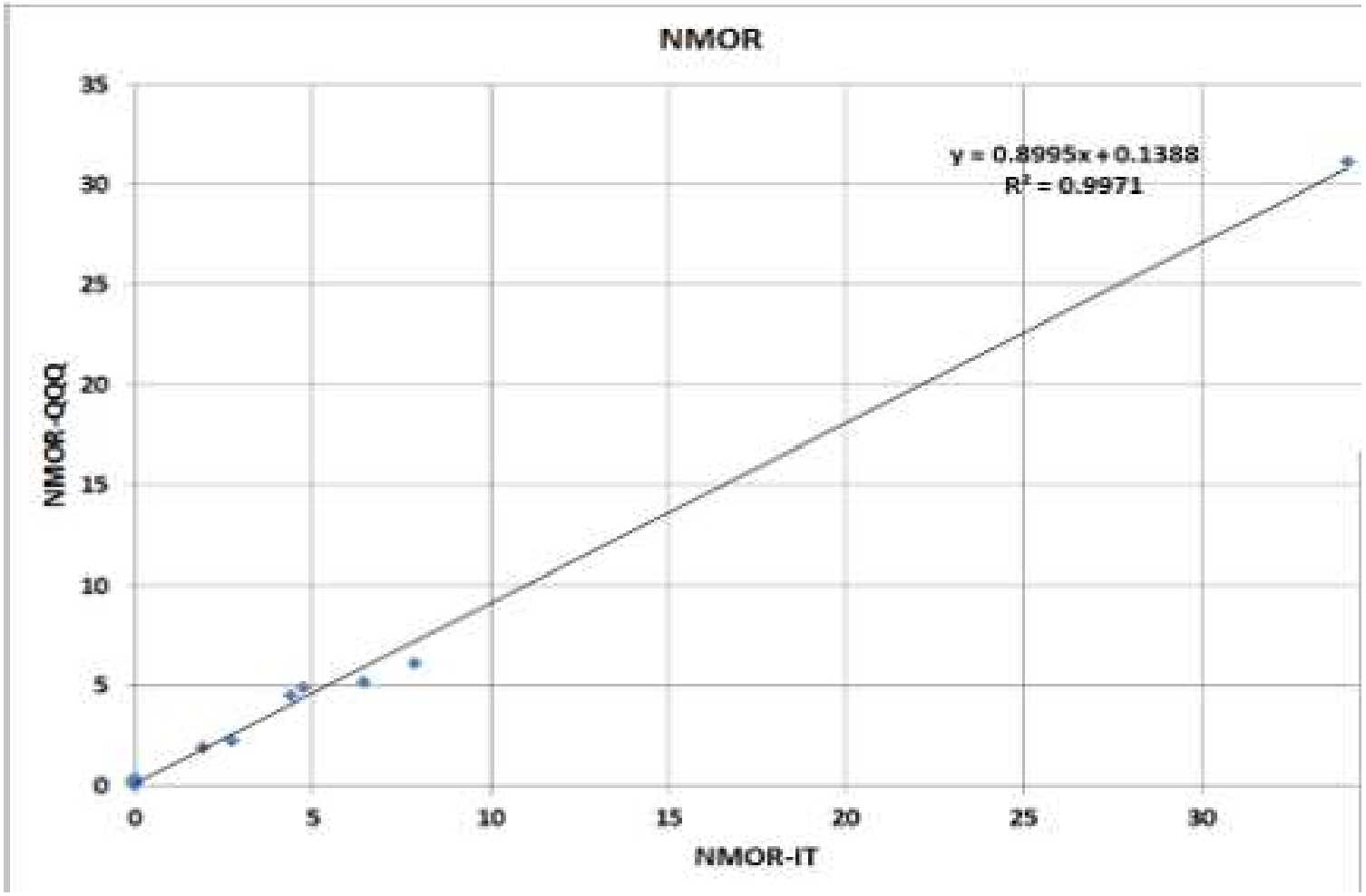


Figure 5: Real Extract Sample Comparison- 0.5 to 35 ppt NPIP

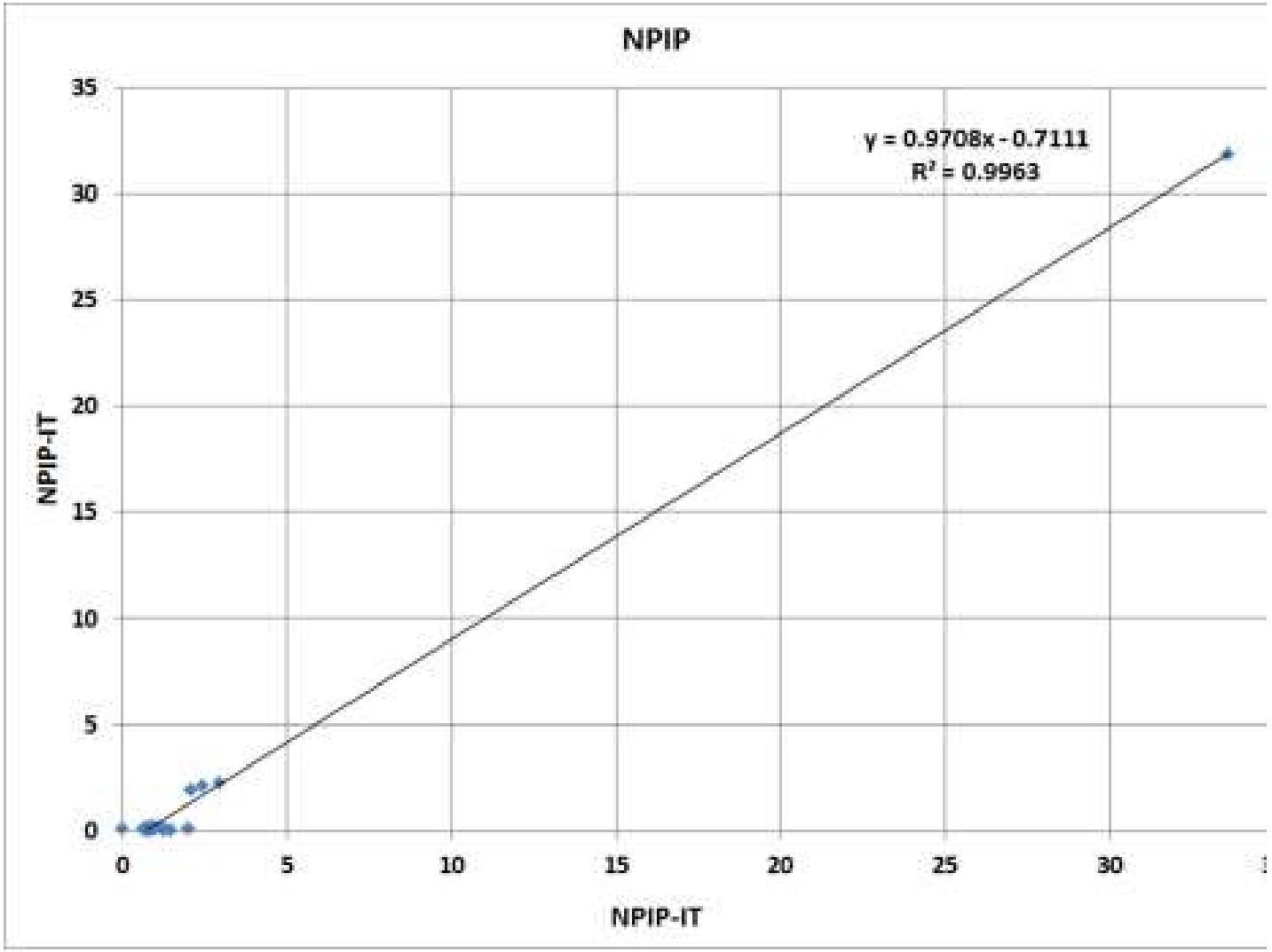
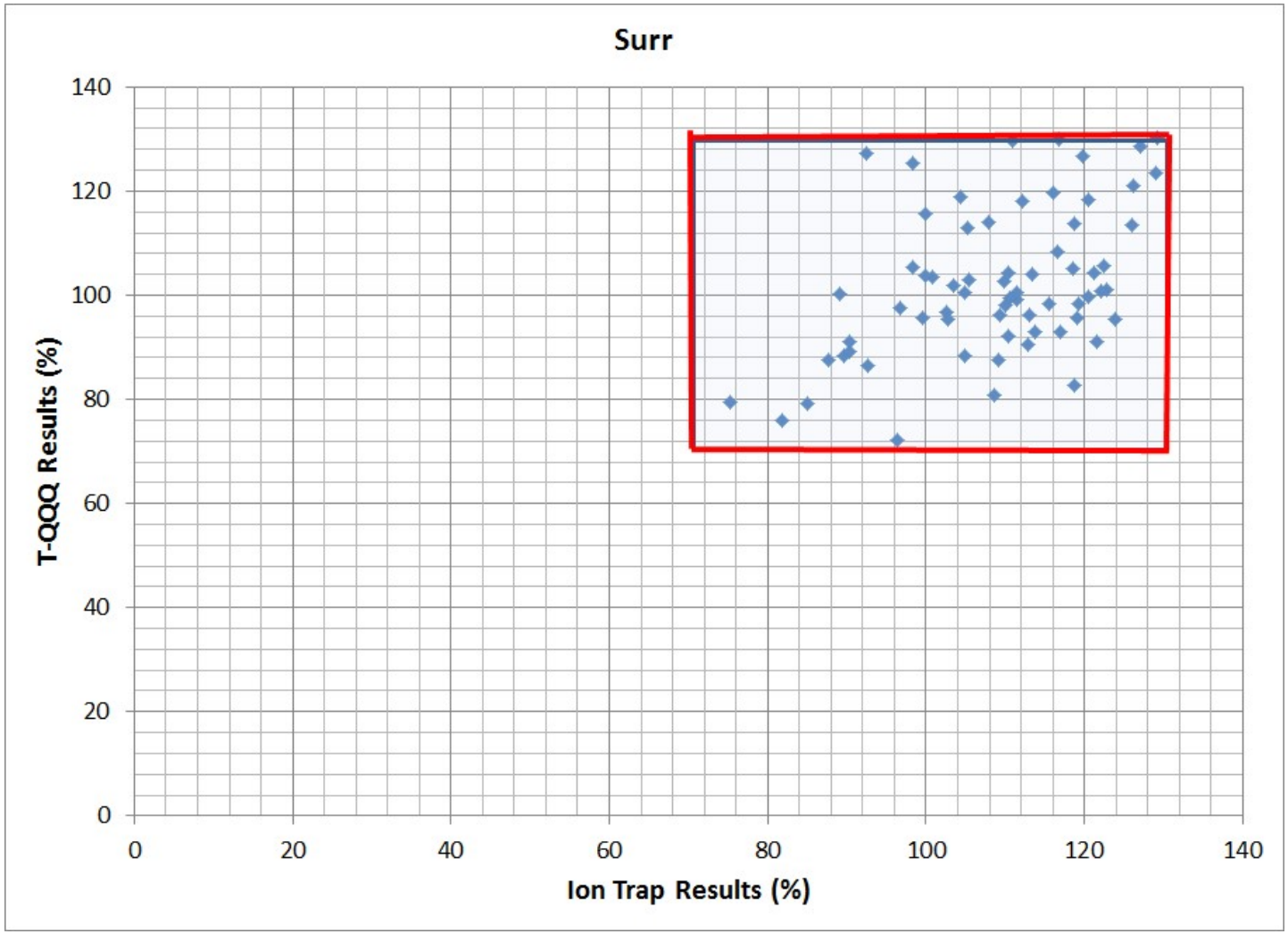


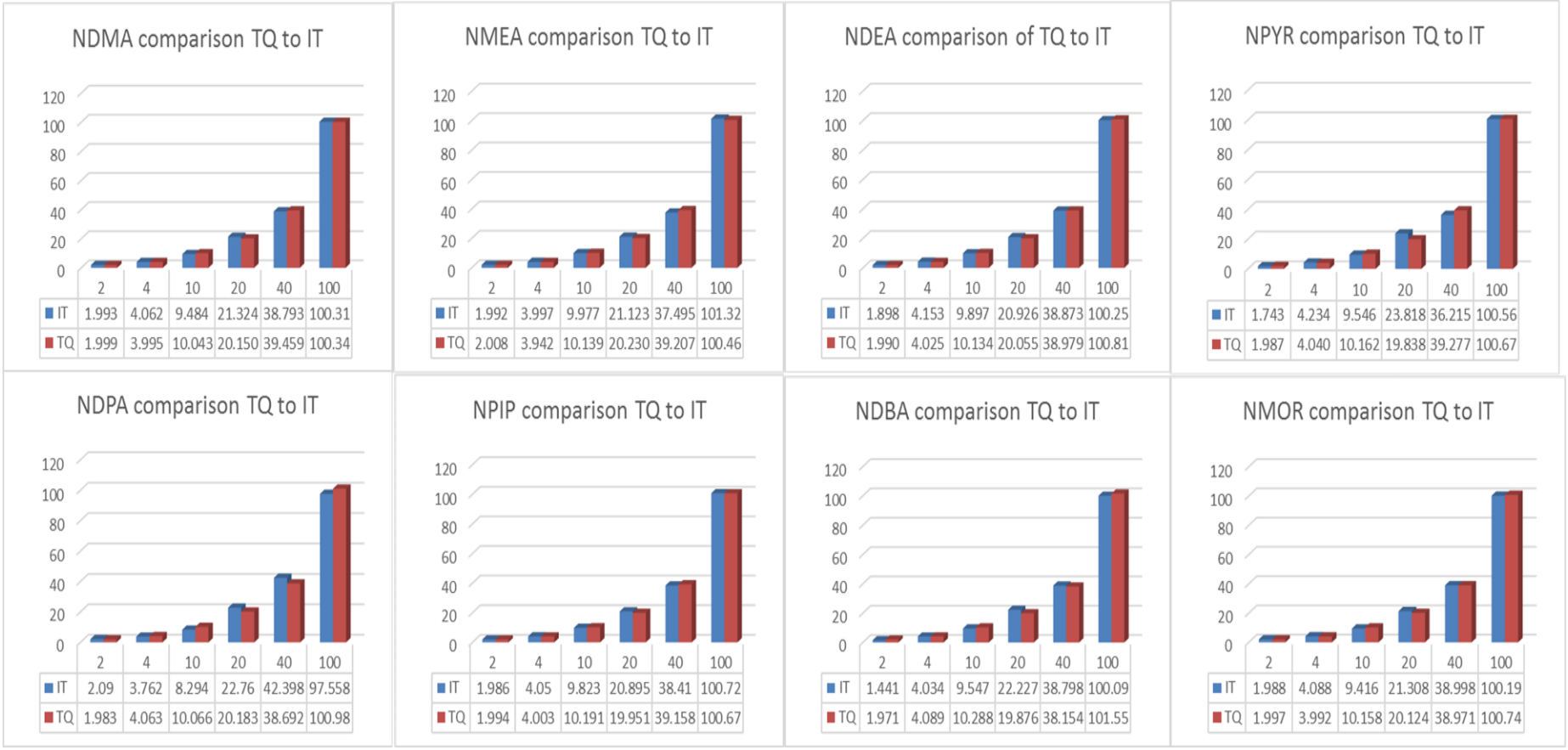
Figure 6: Surrogate Recovery Is Within Limits for Both Methods



Validation

- Real extracted samples(around 400 samples) were run on both the ion trap instrument and TQ
- Samples were run in similar time within holding time
- Used same standards, extraction process and spiking mixes

Figure 7 : Calibration comparison TQ to IT, 2.0 to 100 ppt for extracted sample sets



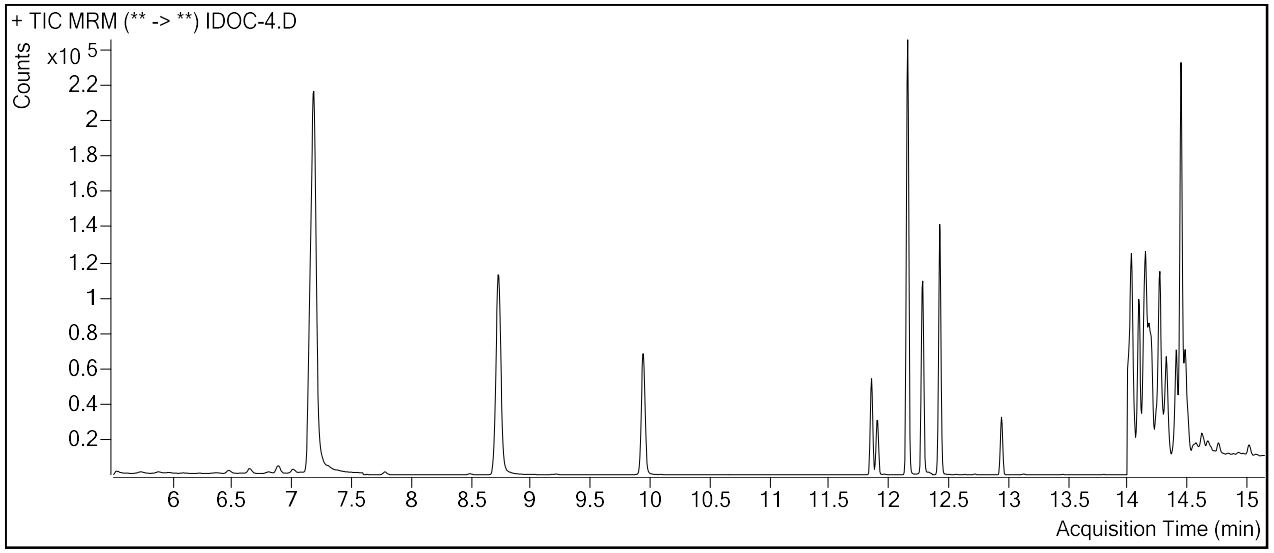
Split Extracted Real Samples for comparison between the Tandem Quadrupole and Ion Trap Instruments

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	1.97	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	0.39	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	0.44	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	139.64	135.64	0.00	0.48	0.00	0.10	1.63	0.00	0.00	0.62	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	0.00	0.51	1.13	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

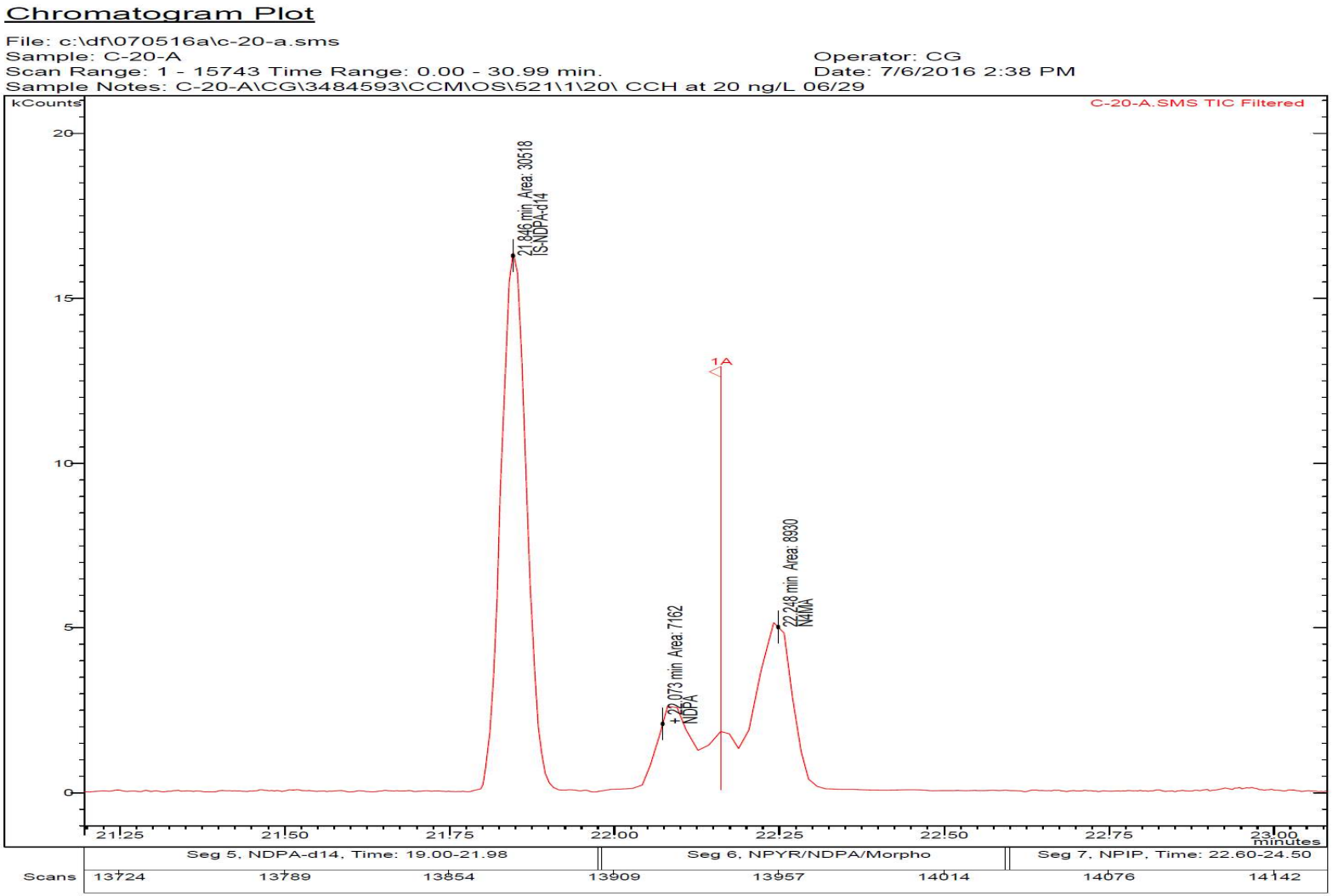
Conclusion- Much Shorter Run Times

Short run time

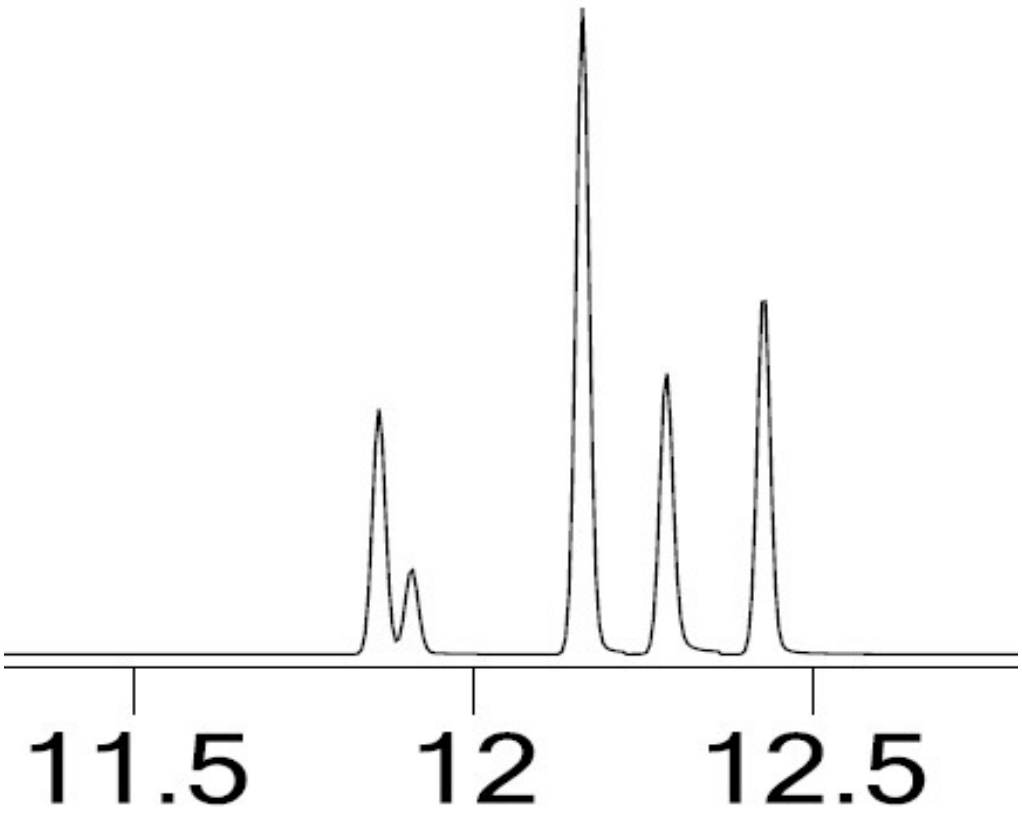
-TQ run time about 15 minutes vs. IT run time about 40 minutes(CI used-Acetonitrile)



Conclusion- Separation for NDPA, NPYR and NMOR-IT with Methanol(Cl) 20ppt 521 std



Conclusion- Better Separation for NDPA, NPYR and NMOR from QQQ-20ppt 521 std



Conclusion – Multiple Advantages to using GC-TQ

- Less injection volume: 1ul Vs. 10ul
- Low maintenance due to EI mode
- Data between TQ and IT shows good correlation

Next Steps

- Analyzing extracts in multiple labs using several different Agilent GC-TQ systems
- Preparation of a new version of 521 (521.1?) based on GC-TQ method.
- Review of complete multi-lab data package by EPA
- Promulgation as an approved method when EPA decides to regulate nitrosamines in drinking waters.

Any Questions?

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