CO_2 Capture Mongstad - Project A – Establishing sampling and analytical procedures for potentially harmful components from post-combustion amine based CO_2 capture

Task 5: Establish Analytical Procedures

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Report	Version	Uploaded
Project A Task 5	Draft Report	15th March 2011
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Project A Task 5	Final	10th May 2011

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EXECUTIVE SUMMARY

Amine A, Task 5 is now completed as far as possible. Some of the methods proved not to be robust in the presence of the likely matrices. It is suggested that more work is required to improve many of the methods. It is evident that matrices have proved to a problem and it recommended that most if not all of the procedures could be improved if better techniques were applied to the removal of the matrices or their effects on the determination of many of the analytes. The research time taken to “prove” these methods would be considerable

The results of analyses from the two commercial laboratories used by CSIRO i.e. Advanced Analytical Australia Pty Ltd and AsureQuality of New Zealand are available. Both commercial laboratories have experience with the handling of solutions containing materials such as nitrosamines and are well aware of the precautions required.

Advanced Analytical Australia Pty Ltd has completed the determination of the analyte groups including the aldehydes, amides, amines and nitrosamines.

AzureQuality have reported values for the alkylamines and nitrosamines.

CSIRO has reported on the determination of ammonia and a group method for nitrosamines and specific methods for the nitrosamines, N-nitrosodiethanolamine and N-nitrosopiperazine. It was unfortunate that the GC-MS-MS at Lucas Heights (because of operational issues) could not be utilised for this project. Thus the methods used by CSIRO utilise techniques such as HPLC and LC-MS-MS (available at Newcastle).

1 INTRODUCTION

This report

The requirements for this task on the establishment of analytical procedures as detailed in the original contract. They are:

“The task is to establish validated methods for chemical analyses of amines and degradation products” (see Table 1.1). “Special emphasis should be on N-nitrosamines and alkylamines.

For nitrosamines, the proposed procedures should include the following 3 approaches and 3 sample types

- A quantitative method for specific N-nitrosamines with relevance in amine studies. Best sensitivity is prioritised
- A screening method where all N-nitrosamines in the sample will be detected and quantified
- A group method giving the total amount of the N-Nitrosamines” (see Ding et al., 1998).

The SOW further includes testing of the chemical analysis methods developed in this study or as defined by Company, with appropriate samples all three sample types.”

The analytes (Table 1) are to be measured (quantified) in the following sample types:

- Treated flue gas
- Wash water from the absorber
- Rich and lean amine solvent

There has been a refocus in this Task as listed on the CMM eRoom, i.e. “Due to time and cost constraints the CCM project would like to make the following prioritization for the rest of the work in subtask 5 under call-off 1.

• Matrix, focus on
- flue gas
- wash water
- (and less on solvent)

• Parameters, focus on
- amines (solvent)
- alkylamines
- nitrosamines
- (and less on ammonia, aldehydes and amides)

• Methods for nitrosamines, focus on
- quantitative and sensitive method
- (and less on group and screening methods)

• Instruments, focus on GC/MS methods but use LC/MS when that is the obvious choice.

We also take the opportunity to remind about the reporting of the developed methods as requested in SOW (ISO 17025 (5.4.4 and 5.4.5), i.e. “a detailed description of the procedure..” and ”a detailed description of the validation..”).”

Compounds (species) of interest are listed in Table 1.1.

Table 1.1. Analytes requested in this task.

Class	**Compound**	**Formula**
Aldehydes	Formaldehyde	CH_2O
	Acetaldehyde	C_2H_5O
Alkylamines	Methylamine	CH_3NH_2
	Ethylamine	$CH_3CH_2NH_2$
	Dimethylamine	$(CH_3)_2NH$
	Diethylamine	$(CH_3CH_2)_2NH$
Amides	Formamide	$HCONH_2$
	Acetamide	CH_3CONH_2
Amines (& Alkanolamines)	Monoethanolamine (MEA)	$H_2NCH_2CH_2OH$
	Diethanolamine	$HN(CH_2CH_2OH)_2$
	Piperazine (PZ)	HNC_4H_8NH
	1,2-Diaminoethane	$H_2NCH_2CH_2NH_2$
	2 Amino-2-methyl-1-propoanol (AMP)	$(CH_3)_2C(NH_2)CH_2OH$
	N-Methyldiethanolamine	$CH_3N(C_2H_4OH)_2$
Ammonia	Ammonia	NH_3
N- Nitrosamines	N-Nitrosodimethyamine	$(CH_3)_2N_2O$
	N-Nitrosodiethyamine	$(C_2H_6)_2N_2O$
	N-Nitrosomorpholine	$C_4H_8N_2O_2$
	N-Nitrosopiperidine (NPIP)	$C_5H_{10}N_2O$
	N-Nitrosodiethanolamine	$(CH_4OH)_2N_2O$
	N-Nitrosopiperazine	$C_4H_9N_3O$
	1-4-Dinitrosopiperazine	$C_4H_8N_4O_2$

The sampling regime has been discussed in the reports of Project A, Tasks 1 and 2 (Halliburton et al., 2010 and Azzi et al., 2010) and the analytical techniques that could be applied to a range of samples taken from the plant (not only the exhaust gas) are detailed in the report of Task 4 (Tibbett et al., 2010). The findings in these reports are generally applicable to the discussions in this report.

General and Sampling

The sampling design although not part of Task 5 is an integral part of an analysis scheme. It is well known that the design of the sampling system is reliant on knowledge of the physical and chemical characteristics of the analytes. The nature of sampling systems and materials of construction are discussed more fully in the reports of Task 1 (Halliburton et al., 2010) and Task 2 (Azzi et al., 2010). The USEPA, 1997, http://www.epa.gov/ORD/NRMRL/pubs/625r97001/625r97001.pdf) describes the two important processes when monitoring emissions from stationary sources and these are applicable to the emissions from a CCM type PCC plant:

- Extraction of a representative sample
- Analysis of that sample for the analytes of interest.

Note that few data from commercial laboratories have been received at the time of drafting – methods that are confirmatory or complimentary to the methods detailed below will be reported. These analytes (listed in Table 1.1) together with their methods of determination are detailed in the Sections 2-5.

References

Note that the website listed below and in the text above was accessed in March, 2011.

Azzi, M, Day, S., French, D., Halliburton, B., Jackson, P., Lavrencic, S. Riley, K. and Tibbett, A. (2010). CO_2 Capture Mongstad - Project A – Establishing sampling and analytical procedures for potentially harmful components from post-combustion amine based CO2 capture, Task 2: Procedures for Manual Sampling, EP 105456, CSIRO, Australia.

Halliburton, B., Day, S., Lavrencic, S., Riley, K. and Azzi, M. (2010). CO_2 Capture Mongstad - Project A – Establishing sampling and analytical procedures for potentially harmful components from post-combustion amine based CO_2 capture. Task 1: Design of Sampling Points for Treated Flue Gas. EP 104693, CSIRO, Australia.

Tibbett, A., Day, S and Azzi, M. (2010). CO_2 Capture Mongstad - Project A – Establishing sampling and analytical procedures for potentially harmful components from post-combustion amine based CO_2 capture. Task 4: Literature Survey of Analytical Procedures and Recommendations; EP 105542, CSIRO, Australia.

United States Environmental Protection Agency, (1997). Handbook - Continuous Emission Monitoring Systems for Non-criteria Pollutants, EPA/625/R-97/001, 169 pages.
http://www.epa.gov/nrmrl/pubs/625r97001/625r97001.pdf
http://www.epa.gov/ORD/NRMRL/pubs/625r97001/625r97001.pdf

2 DETERMINATION OF AMMONIA

Title: Quantitative method for Ammonium ion in aqueous post-combustion capture matrix using Ion Chromatography

Authors: CSIRO (specifically A. Allport, P. Jackson, M. Attalla).

Introduction: This method utilises an ion chromatography column for separation of the analyte ammonium ion from the matrix. The system consisted of a Dionex IC-3000 coupled with a Dionex AS auto-sampler for sample delivery. The ion column employed was a Dionex CS16 cation column and methanesulfonic acid (MSA) was used as eluent. The system was run in an isocratic mode.

Warnings: *PCC liquors may contain N-nitrosodiethanolamine (NDELA, CAS-1116-54-7) and/or N-nitrosomorpholine (NMOR, CAS 59-89-2), both potential carcinogens and appropriate precautions (e.g. wearing appropriate PPE, sample manipulations in a certified fume hood) should be exercised when handling the reference solid, any reference solution or PCC liquors.*

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Scope: This method is for the quantitative determination of ammonium ions in waters, wash-waters or PCC liquors. It is a requirement of this method that samples containing PCC liquors are diluted 1/200-1/1000. This dilution reduces the effect of tailing observed when high concentrations of an analyte are present in a sample during IC elution. Tailing masks the signal for other analytes present in the sample and in this case masks the signal of interest, that of the ammonium ion. The limit of detection (LOD) has been determined as the mean blank value plus three

□blank S.D. fo

has been determined as the mean blank value plus 10 x blank S.D. for six blank runs. Blank runs consisted of a 300 ppm MEA aqueous solution. The results obtained for peak area of six blank runs is presented in Table 2.1.

Table 2.1. LOD/LOQ for Ammonium in aqueous 300ppm MEA.

	Peak Area µS*min
	0.00383
	0.00366
	0.00363
	0.00383
	0.00434
	0.00401
Mean	0.00388
S.D.	0.00026
LOD	0.00467
LOQ	0.00651

Within this work the limit of detection and limit of quantification for ammonium in aqueous MEA 300 ppm using IC are both 0.2 ppb when rounding is appropriately applied.

Definitions

IC ion chromatography
LOD limit of detection
LOQ limit of quantification
MEA Monoethanolamine
MSA methanesulfonic acid
S.D. standard deviation

Materials

Ammonium Chloride ≥ 99.5% CAS 1225-02-9
Monoethanolamine (MEA) ≥ 98% CAS 141-43-5
Charcoal-filtered water (R >18 M □□

Experimental conditions for analysis of Ammonium ion in an MEA matrix

Instrumentation: IC (Dionex ICS-3000)
Chromatography Column: Dionex CS16, 250mm
Column temperature: 60ºC
Cell Heater: 35ºC
Suppressor Type: Dionex CSRS 2mm
Suppressor Current: 22mA
Eluent flow mode: Isocratic
Eluent: Methanesulfonic acid (MSA)
Eluent Flow rate: 0.36mL/min
Eluent Concentration: 10.00mM
Test sample injection volume: 10µL
Programme Duration: 25min

Calculations

Linearity

Ammonium standards were prepared from a stock aqueous ammonium chloride solution of 10 ppm of ammonium. 1mL aliquots containing 0.5, 2, 5, 10, 20 ppb of ammonium were prepared in aqueous MEA 300 ppm for calibration of the method. A plot of ammonium peak area vs. concentration of ammonium in ppb yields a linear relationship passing through the origin with correlation coefficient of 0.999. (Figure 2.1.).

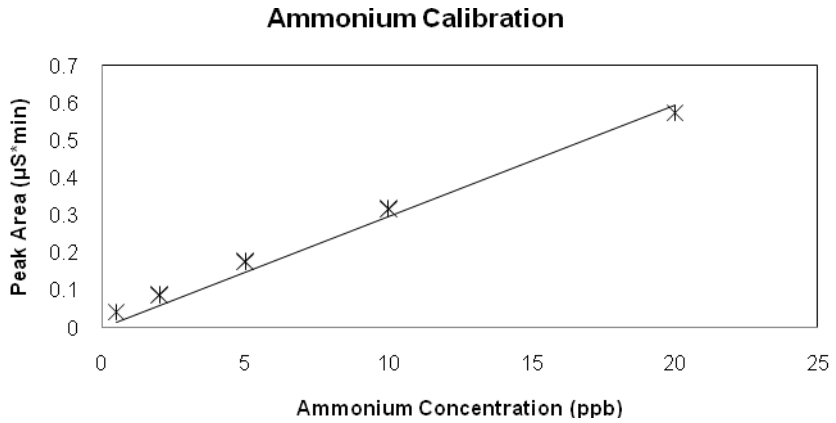


Figure 2.1. Linear calibration plot of peak area (µS*min) vs. ammonium concentration (ppb)

Repeatability
Six samples containing 8 ppb of ammonium in aqueous MEA 300 ppm were analysed to determine repeatability. A tabulation of the data collected along with mean, standard deviation and 95% confidence interval is displayed in Table 2.2.

Table 2.2. Table of Peak area, mean, standard deviation and 95% confidence intervals for 8ppb ammonium in aqueous MEA 300 ppm.

	Peak Area µS*min
	0.286
	0.286
	0.287
	0.288
	0.287
	0.286
Mean	0.287
S.D.	0.001
1.96S.D.	0.002
95% CI +	0.289
95% CI -	0.285

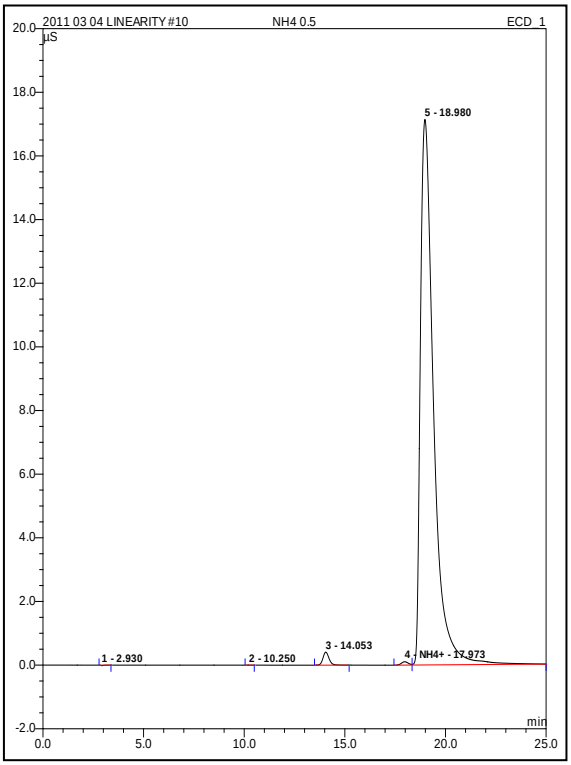
Blind Spike trial/recovery test
To test for matrix effects on the developed method 6 test samples were prepared from 30% wt MEA aqueous solutions with a loading of 0.45 mol CO_2/mol amine and diluted 1/1000 and tested using the developed method. Before testing two of the test samples were spiked with Ammonium to give a final ammonium concentration of ~ 10.0 ppb. A standard of 10 ppb Ammonium in aqueous MEA 30mg/L was also prepared for reference.
No significant matrix effects were observed when the test samples and reference were tested against the established method. The reference sample returned an Ammonium concentration

of 10.7 ppb while the test samples returned an ammonium concentration of 10.9 and 10.9 ppb.

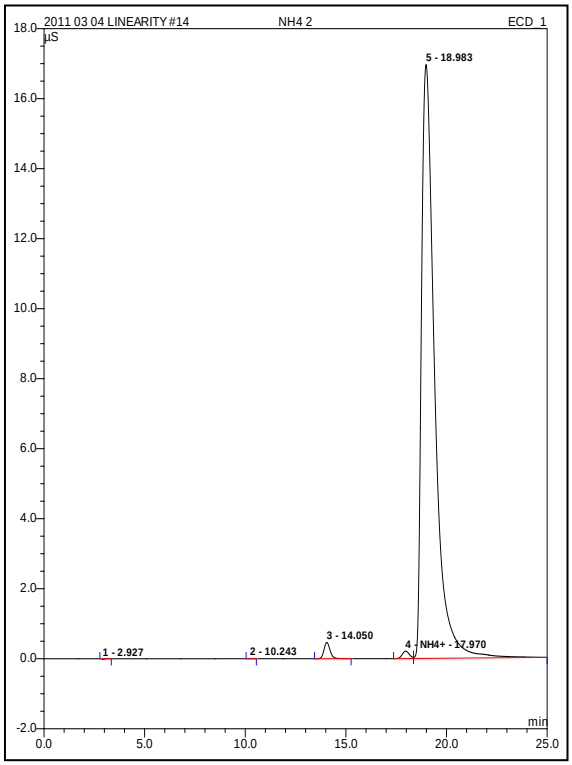
Summary
The quantitative determination of ammonium in this method is achieved through the use an ion chromatography column for separation of the analyte ammonium from the matrix. A good separation between the different components is achieved using a solution of 10 mmolar methanesulfonic acid at a flow rate of 0.36mL/min. A five point calibration was completed for ammonium with the correlation coefficient being 0.999 and a repeatability of ±0.5%.

Calibration Chromatographs

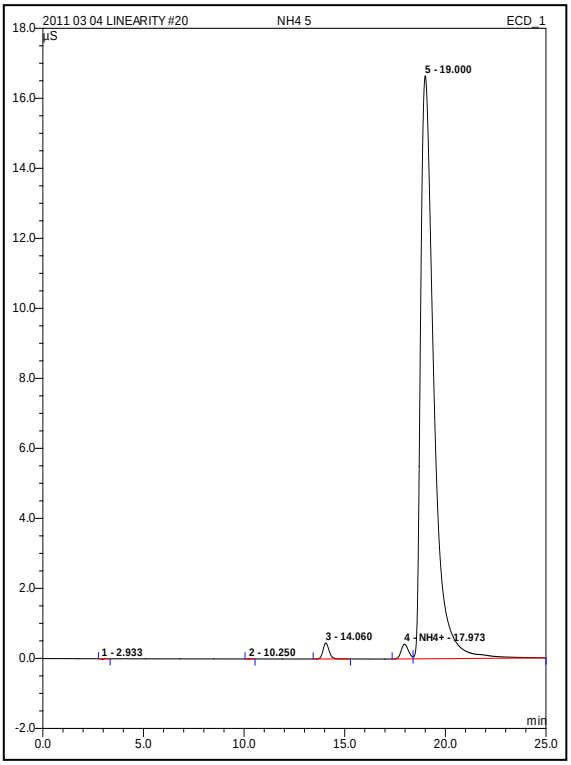
a)



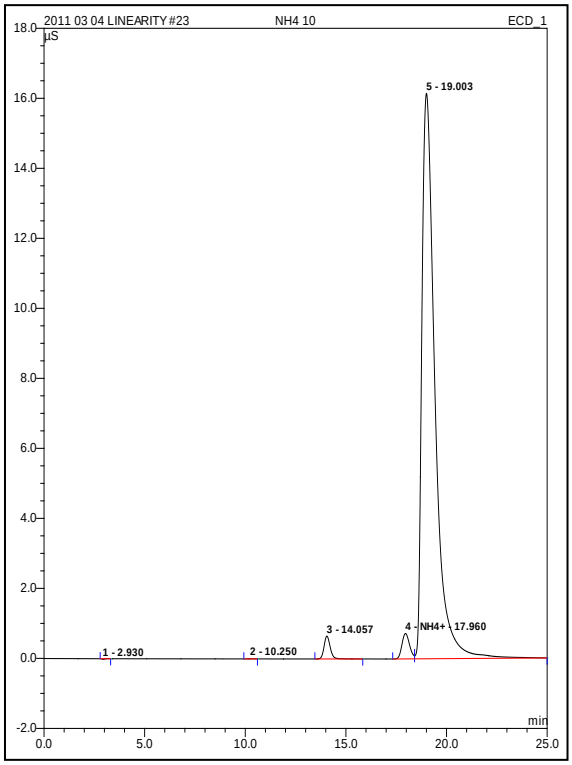
b)



c)



d)



e)

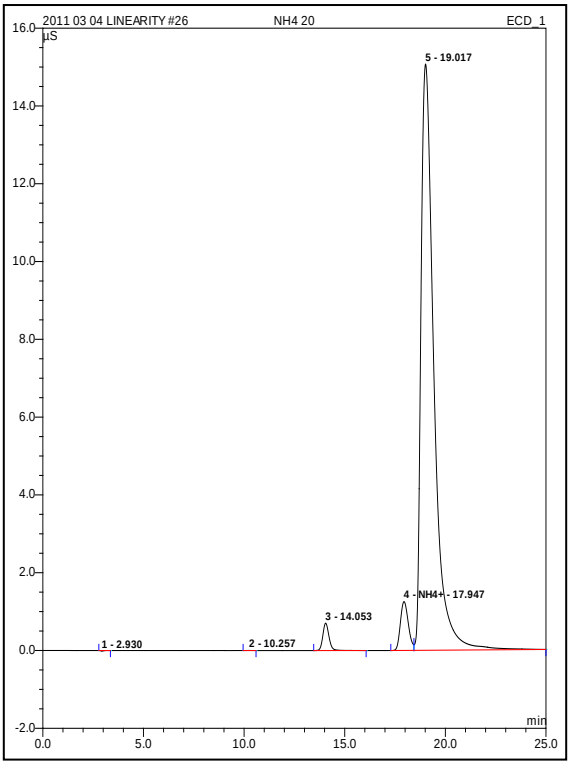


Figure 2.2. continued Chromatographs produced for calibration of method a) 0.5 ppb NH_4^+ in aqueous MEA 300ppm b) 2 ppb NH_4^+ in aqueous MEA 300ppm c) 5 ppb NH_4^+ in aqueous MEA 300ppm d) 10 ppb NH_4^+ in aqueous MEA 300ppm e) 20 ppb NH_4^+ in aqueous MEA 300ppm.

3 GROUP METHOD FOR THE DETERMINATION OF TOTAL N-NITROSAMINES

Title: Group method for the determination of total N-Nitrosamines

Authors: CSIRO (specificially Robert Rowland, Phil Jackson and Moetaz Attalla)

Scope: This method is for the determination of total N-Nitrosamines in wash waters and PCC liquors.

Summary: The nitroso group of an N-Nitrosamine can be chemically removed by reaction with hydrobromic acid dissolved in glacial acetic acid. The nitroso group evolves from the solution as nitric oxide. This nitric oxide can then be detected using an oxides of nitrogen gas analyser (NO_x analyser). PCC liquors and wash waters are prepared for denitrosation by solvent extraction. The solvent extraction is used to remove nitrite and the majority of the sample matrix prior to denitrosation.

The denitrosation is carried out in refluxing 1,2-dichloroethane at 83°C, with chemiluminescence detection of the produced nitric oxide (see Fig. 3.1).

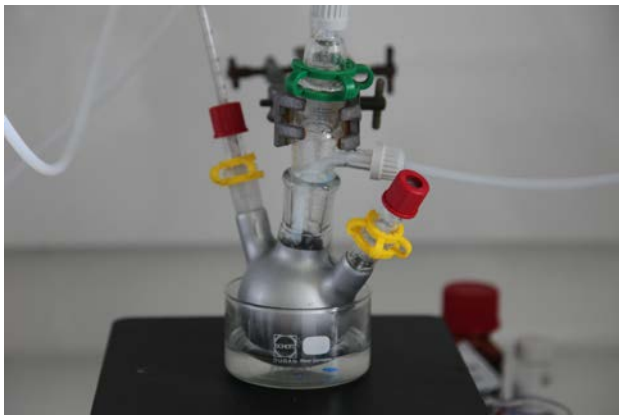


Figure 3.1. Picture of the denitrosation reaction vessel.

Warnings:
N-Nitrosamines are possible carcinogens and appropriate precautions must be taken.1,2-dichlroethane is highly flammable, may cause cancer, is harmful if swallowed, and is irritating to eyes, respiratory system and skin. It should be used with appropriate caution. When heating this solvent it should always be done in an inert atmosphere.Dichloromethane has shown limited evidence as a carcinogen. Glacial Acetic Acid may cause severe burns and is flammable.Hydrobromic acid causes burns and is irritating to the respiratory system.
Acetic Anhydride is flammable and is harmful by inhalation or swallowing.
All handling of these compounds should be conducted by trained personnel in an accredited fume cupboard with the appropriate gloves, lab coat and safety glasses.

Materials:

Reagents:
1,2 – dichloroethane anhydrous 99.8% (Sigma Aldrich)
Dichloromethane CHROMASOLV plus ≥99.9% (Sigma Aldrich)
Hydrobromic Acid 48% ACS Reagent (Sigma Aldrich)

Glacial Acetic Acid (Sigma Aldrich)
Acetic Anhydride (Fluka)
N-Nitrosopiperazine (Sigma Aldrich)
N-Nitrosomorpholine (Sigma Aldrich)
Ultra High Purity Argon (BOC Australia)
Dry Nitrogen gas
0.1M & 1M potassium hydroxide solutions
Ice
High purity water (18 MΩ)
Sodium sulphate anhydrous (Dried at 150°C)
Sodium chloride AR grade

Apparatus (general):
Solvent Extraction Procedure
Separating funnels 50mL
Amber glass PYREX bottles 50 and 100mL
Aluminium foil (for reducing sample UV exposure in separating funnels)
Retort stands and rings
Assorted beakers and measuring cylinders
pH strips 0-14.
5mL pipettor and tips

Apparatus for Denitrosation Procedure
Three necked 100mL round bottom flask (painted silver)
150ml Petri dish
One mass flow controller
One magnetically stirred hot plate
8mm PTFE coated stirrer bars
1 thermometer (6-7mm O.D.)
¼ inch PTFE tubing
2 x ¼ turn stainless steel ball valves (Swagelok)
Quickfit 80mL test tube and dreschel bottle head to fit (solvent trap)
Thermos flask
2 x Quickfit 14/23 screw thread adaptors to fit 6-7mm tubing
1 x Quickfit 24/29 screw thread adaptor to fit 6-7mm tubing
1 x Quickfit 24/29 adaptor with screw thread sidearm for 6-7mm tubing
PTFE coated septa
14/23 and 24/29 joint clips
Gas tight syringes 250µL, 5mL & 10mL
Syringe needles for sample injection
Oxides of nitrogen gas analyser in nitric oxide mode (0-20ppm)
Regulator for argon gas cylinder (output pressure ~200kPa)
PC and data logging equipment.
Software to integrate peaks (e.g. Origin)

Method:
Solvent Extraction Procedure
Take 20mL of sample and adjust the pH value to 10 drop wise using conc. KOH solution
Transfer the resulting mixture to a 50 ml separating funnel and extract with 3 x 20 ml aliquots of dichloromethane for 5 minutes each.
Retain the organic layer, and evaporate under a stream of nitrogen (N_2) gas to a volume of 5 ml. Dry anhydrous Na_2SO_4 can be used to dry the DCM at this step.
Transfer the DCM solution (5 ml) to a clean 50 ml separating funnel.

Extract with 3 x 10 ml aliquots for 5 minutes each with high-purity water (18 MΩ). Discard the organic layer (with due consideration to the environment), and evaporate the aqueous layer under N_2.
Add 5.0mL of 1,2-dichloroethane. Shake well.
Denitrosation Procedure
Transfer 30mL of 1, 2-dichloroethane to a clean dry 100mL round bottom flask, add 2mL of denitrosation reagent, place on denitrosation apparatus (Figure 3.1. and 3.2.) and purge with 0.3 L/min of ultra high purity (UHP) argon for 5 minutes.
Close off the argon gas flow to the reaction vessel by switching the gas flow to bypass. Bring contents to refluxing temperature of 83°C.
Open argon gas flow to the reaction vessel.
Inject 100 -2000 µL of sample through septum.
Record nitric oxide peak and integrate area under the curve.
Denitrosation Reagent
Dilute 1.7mL of 45% hydrobromic acid to 25mL with glacial acetic acid; add 2ml of acetic anhydride.

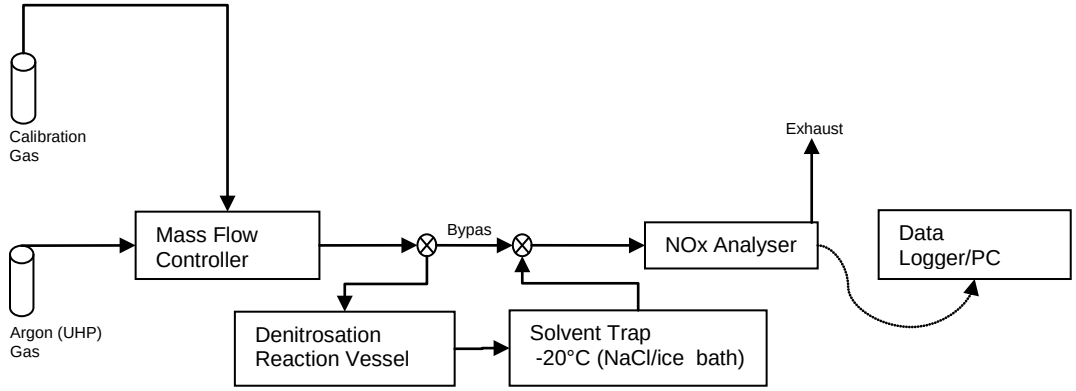


Figure 3.2. Schematic of denitrosation apparatus

Linearity:
Aliquots of 1,2-dichloroethane containing 50, 100, 200, 500 and 1500 nmol of N-nitrosopiperazine were used for calibration of the denitrosation procedure. See Table 3.1.

Table 3.1. Calibration Data (blank corrected).

N-Nitrosopiperazine (nmol)	Peak Area (ppm.s)
0	0.0
50	72.3
100	168.1
200	413.6
500	975.7
1500	3253.6

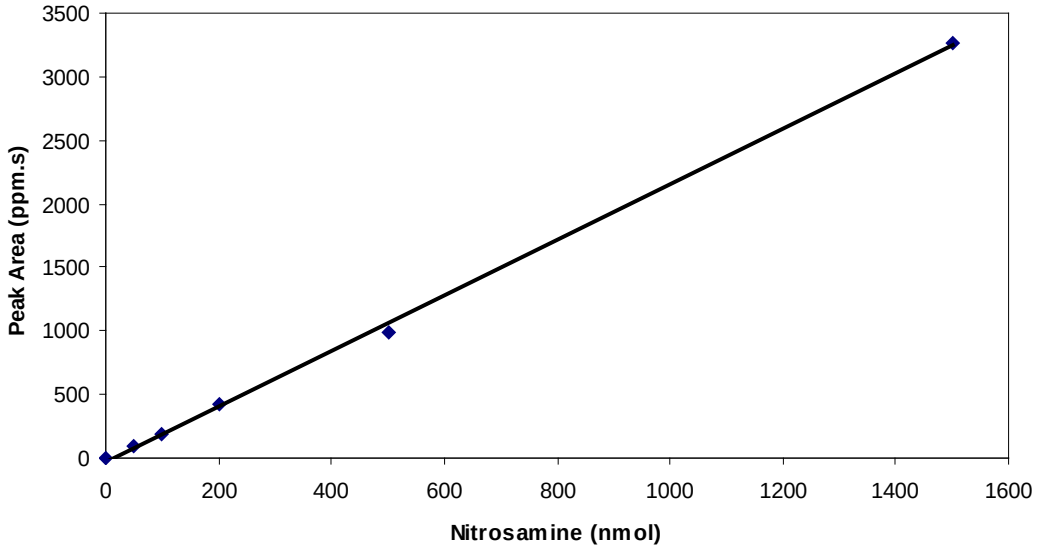


Figure 3.3. Linear calibration plot of peak area vs. amount of nitrosamine (Nitrosopiperazine).

Table 3.2. Regression data for calibration.

Slope	2.181
Intercept	-40.145
RSQ	0.9990

Limit of Detection

The limit of detection has been determined as three times the standard deviation of the noise in six blanks (100µL of 1,2-dichloroethane).

Table 3.3. Limit of detection data for denitrosation procedure.

	Peak Area (ppm.s)
Blank 1	15.14
Blank 2	14.70
Blank 3	14.47
Blank 4	14.20
Blank 5	12.36
Blank 6	15.31
Mean =	14.36
SD =	1.07
3SD =	3.20
LOD	20 nmol

The linear range of the denitrosation procedure is 20 – 1500nmol.

Table 3.4. Working concentration range for denitrosation with the solvent extraction procedure

	Injection Volume (mL)	N-Nitrosamine Concentration (µmol/L)
LOD	2.00	3
Maximum Concentration	0.100	3750

Repeatability:
Six injections of 200 nmol of NPz in 1,2-dichloroethane were analysed. The NO spectra for these are shown in Figure 3.4.

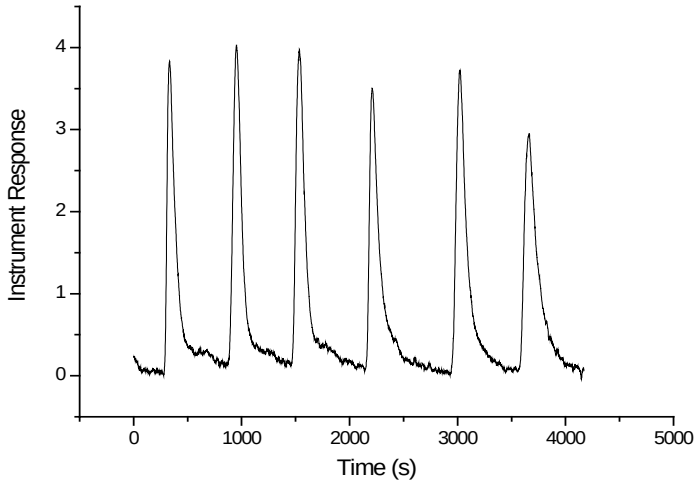


Figure 3.4. Six replicate injections of 200 nmol of NPz.

Table 3.5. Table of peak areas, mean, standard deviation and 95% confidence interval recorded for 200nmol of NPz.

Run	Measured Amount (nmol)
1	209
2	203
3	215
4	207
5	222
6	217
Mean	212
Std Dev.	7.1
95% Confidence Interval (±%)	7

For robustness, 500nmol N-nitrosomorpholine was analysed and the results was determined using the NPz calibration.

Table 3.6. Results from injection of 500nmol of N-nitrosomorpholine

Sample	Result (nmol)	%
500nmol N-Mor	532	105

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Selectivity:
The denitrosation method is highly selective. This is due to the solvent extraction removing a significant portion of the sample matrix, and the denitrosation reagent only reacting with NO containing functional groups. The only serious interference is due to n-alkylnitirtes (Drescher, 1978).

Table 3.7. Uncertainties in the Denitrosation Procedure.

Error Source	Error Magnitude
Repeatability of Measurement	±7%
Sensitivity to different Nitrosamines	±5%

Several more nitrosamines need to be analysed to better determine the difference in sensitivities.

Solvent Extraction Procedure:

The errors introduced by the solvent extraction have yet to be determined. The sample results are listed in Table 3.8.

Table 3.8. Sample Results

Sample	N-Nitrosamine (µmol/L)
ID-A	22
ID-B	<3
ID-C	<3

Definitions:
N-Mor – N-nitrosomorpohline
NPz – N-nitrosopiperazine
Std Dev. – standard deviation

A3 References

Drescher, G.S., 1978. Estimation of extractable n-nitroso compounds at parts-per-billion level. Analytical chemistry (Washington) 50, 2118.

4. QUANTITATIVE METHOD FOR N-NITROSODIETHANOLAMINE (NDELA)

A shortened, precise version of this method is given in Appendix 1 (i.e. without any of "work-up data included).

Title. Quantitative method for NDELA (N-nitrosodiethanolamine) in aqueous post-combustion capture matrix using IC-MRM

Authors. CSIRO (specifically P. Jackson and M.I. Attalla).

Introduction. This method utilises an ion chromatography system with an MS detector for separation of the analyte from the matrix. The MS analysis mode employed is multiple reaction monitoring (MRM). In total, three dissociative transitions are monitored at a common retention time (t_R) for analyte identification, and all three are used for quantitation. Ion chromatography was chosen because typical reverse phase conditions proved to be unsuitable for high concentrations of matrix alkanolamine, with almost complete signal suppression when more than 1 % of the test sample consisted of 30 % w/w 2-aminoethanol (MEA). This is a consequence of two factors (i) inadequate separation of the analyte from the matrix when organic gradients are used, and (ii) the high proton affinity of the matrix (chiefly MEA) which suppresses the co-eluting MS signal of the analyte. The method acknowledges the Schothorst and Somers method for NDELA in cosmetics (Schothorst, and Somers, 2005), but is significantly modified for PCC liquors.

There are two important modifications with respect to Schothorst and Somers (2005) method. First, ion chromatography (rather than a reverse phase C18 column) is employed to achieve separation, and second, three MRM transitions are monitored, instead of two (Schothorst and Somers, 2005). Jackson and Attalla (Jackson, P.; Attalla, M.I. (2010) N-Nitrosopiperazines form at high pH in post-combustion capture solutions containing piperazine: a low-energy collisional behaviour study. Rapid Commun. Mass Spectrom. 24: 3567–3577) have demonstrated that the two major transitions which describe the loss of the nitroso-functional group in N-nitrosopiperazine (loss of NO, 30 Da, and loss of HNO, 31 Da) occur at almost the same energy demand. As a result, the abundance of the product ions (M/z 85, M/z 86) varies unpredictably over a small collision energy range that might typically be used in tandem mass spectrometry experiments. While the implications have not been fully explored for NDELA, monitoring just a single transition may not be suitable for quantitation purposes. For this reason both losses of NO and HNO are monitored (as a sum to represent total loss of the NO functional group). This also eliminates any uncertainty that could arise from instrument cross-talk. Cross-talk is problematic in low-resolution tandem mass spectrometry instruments when the DC:RF ratio is relaxed (lower DC) to maximise sensitivity. When two transitions are separated by less than 1 M/z unit, this situation can be exacerbated.

Warning. *N-nitrosodiethanolamine (NDELA, CAS-1116-54-7) is a potential carcinogen and appropriate precautions (e.g wearing appropriate PPE, sample manipulations in a certified fumehood) should be exercised when handling the reference solid, any reference solution or PCC liquors.*

Scope. This method applies to waters, wash-waters or PCC liquors with the following caveat. A portion of typical 300 mg/g PCC liquor (test sample) shall be diluted using charcoal-filtered water (R > 18 MΩ) by a factor of at least 1/20, preferably by 1/40-1/100. This is done to avoid a reduction in sensitivity arising from MEA as described in the Introduction. Suspended solids should be removed from any test sample using pelletization (e.g. by low speed

centrifugation), prior to dilution. Test portions of water- and wash-water samples can be analysed without dilution after centrifugation.
Definitions of limit-of-detection (LOD) and limit-of-quantitation (LOQ), as described in the ISO normative reference 2, are too prescriptive for application to trace detection using sophisticated instrumental methods; see normative reference 3 (N3). In this article (N3), two approaches to determining LOD are described: a statistical method (mean + 3 $\times$ S.D., number of blank samples = 6) and an empirical method. The empirical method entails serial dilution of the reference standard; increasingly dilute reference samples are then analysed until the measurable (associated with the analyte) is no longer distinguishable from the baseline. A LOD of 22 ng/ml (ppb) is obtained empirically (for all transitions) in water. The results obtained using the statistical method for NDELA in water are presented in Table 4.1. The statistical LOQ is defined as the mean + 6 $\times$ S.D.'s (number of blank samples = 6).

Table 4.1. Statistical LOD/LOQ for NDELA in water using IC-MRM.

Transition	**LOD**		**LOQ**	
	Peak area	**[NDELA], ppb**	**Peak area**	**[NDELA], ppb**
135 $\rightarrow$ 74	351	**10**	743	**23**
135 $\rightarrow$ 104	219	**37**	380	**56**
135 $\rightarrow$ 105	226	**55**	401	**87**
Total NO loss	397	**41**	621	**57**

The empirical limit of detection for NDELA in charcoal-filtered water (R > 18 MΩ) using HPLC-MRM-MS (MeOH/H_2O mobile phase, similar MS conditions) is between 3-7 ppb in our laboratory. As discussed in A5.2, separation of NDELA from the MEA matrix in PCC liquors was ineffective using reverse-phase HPLC. While reverse-phase HPLC-MS does not appear to be suitable for NDELA in PCC liquors, it may be a viable alternative for wash- and discharge waters with lower amine concentrations ([$MEA_{(aq)}$] < 2 mg/ml, 2000 ppm).

Normative references and bibliography.

Chemistry – Layouts for standards – Part 2. Methods of chemical analysis. International Standards Organisation document ISO 78-2:1999(E).

Accuracy (trueness and precision) of measurement methods and results – Part 1: General principles and definitions. International Standards Organisation document ISO 5725-1:1994(E).

Armbruster, D.A.; Tillman, M.D.; Hubbs, L.M. (1994) Limit of detection (LOD)/Limit of quantitation (LOQ): Comparison of the empirical and statistical methods exemplified with GC-MS Assays of abused drugs. Clin. Chem. 40: 1233-1238.

General requirements for the competence of testing and calibration laboratories. International Standards Organisation document ISO 17025:2005(E).

Definitions.

NDELA	*N-nitrosodiethanolamine*
IC	*Ion chromatography*
MRM	*multiple reaction monitoring*
HPLC	*high performance liquid chromatography*

PCC	*post combustion capture*
MS	*mass spectrometer*
Transition	*reproducible fragmentation or dissociation of mass-selected analyte [M+H]+ induced by collision with an inert gaseous target under specified conditions*
DC:RF	*ratio of direct current (DC, resolving) selectively superimposed on radio-frequency (RF) current and applied to quadrupole rods to control the stability of certain ion orbits (with selected M/z ratio) within the quadrupole, such that the ion motion satisfies the Mathieu equations*
LOD	*limit of detection*
LOQ	*limit of quantitation*
σ_M	*mean/(N)$^{1/2}$, where N = number of measurements or samples, or sample size*
S.D.	*standard deviation*
C.I.	*confidence interval*

Reagents

Water, CAS 7732-18-5, purified to compliance with ASTM (D1193-91) Type 1*, R > 18 MΩ/cm
Formic acid, CAS 64-18-6, > 99 %
Acetonitrile, CAS 75-05-8, HPLC grade
2-aminoethanol (MEA), CAS 9007-33-4, > 99 %
Oxalic acid, CAS 144-62-7, > 99 %
Potassium nitrate, CAS 7757-79-1, > 99.0 %
Sodium sulphate anhydrous, CAS 7757-82-6, > 99 %
Sodium bicarbonate, CAS 144-55-8, > 99.5 %

Experimental conditions for standardisation of NDELA in an aqueous matrix.

Test sample injection volume: 40 µl
Instrumentation: LC-MS/MS (Waters Acquity MS^2)
Ion mode: Positive ion electrospray
MS operation mode: multiple reaction monitoring (MRM)
Capillary voltage: 3.57 kV
Cone voltage: 38 V
Extractor: 2.0 V
RF: 0.2 V
Source temperature: 150 °C
Desolvation temperature: 350 °C
Desolvation gas flow rate: 500 L/hr
Collision gas flow rate: 0.03 ml/min
Transition dwell time: 0.1 s
Interscan delay: 0.02 s
Inter-channel delay: 0.02 s
MS1 low mass resolution: 14.0
MS1 high mass resolution: 14.0
MS3 low mass resolution: 13.5
MS3 high mass resolution: 13.5
MS analyser baseline pressure: $< 1.3 \times 10^{-5}$ mbar
MS analyser pressure after admission of collision gas: $1.2\text{-}1.3 \times 10^{-3}$ mbar
Collision gas: high purity argon
T-cell bias: 12 V
Multiplier voltage: -645 V
Run time: 25 mins
Transitions:

(i) 135.1 → 74.2
(ii) 135.1 → 104.1
(iii) 135.1 → 105.1
Peak height or peak area used: Peak area
Smoothing prior to peak integration: Mean of 5 scans
Column: Dionex CS16 3 × 250 mm
Column temperature: 20 °C
Injection volume: 40 μl
Solvent flow rate: 0.3 ml/min
Mobile phases: A = 100 % MeCN (LC-MS grade, Sigma Aldrich), B = 1.2 % aqueous HCOOH (HCOOH, LC-MS grade, Sigma Aldrich)
Gradient:

Table 4.2. IC-MRM gradient conditions

Time (mins)	A %	B %
0.00	85.0	15.0
10.00	85.0	15.0
12.00	1.0	99.0
16.00	1.0	99.0
18.00	99.0	1.0
22.00	99.0	1.0
23.00	85.0	15.0
25.00	85.0	15.0

NDELA standard material: purchased from Sigma Aldrich, purity > 90 %. Major contaminants: isopropanol and diethanolamine.
Standard NDELA solution = 22.9×10^{-3} g NDELA added to 10 ml charcoal-filtered water (R > 18 MΩ). [NDELA] = 2.3 ± 0.2 milligrams/millilitre.
Total solution mass = 10.0229 g
This solution was used to evaluate the performance of NDELA quantification in all matrices. Hereafter it is referred to as the reference solution.
t_R (NDELA) ≅ 4.0 mins

Calculations:

Linearity
Linear regression results for a series of dilutions of the reference solution in charcoal-filtered water are presented in Table 4.3. [$NDELA_{(aq)}$] = 22.9×10^{-9} g/ml, 45.8×10^{-9} g/ml, 229×10^{-9} g/ml, 458×10^{-9} g/ml, 2.29×10^{-6} g/ml, 4.58×10^{-6} g/ml.

Table 4.3. Standard regression results for a serial dilution of the reference solution in charcoal-filtered water.

	135 → 74	**135 → 104**	**135 → 105**	**Total NO loss**
Slope	32290 ± 616.7	8709 ± 147.9	5539 ± 88.32	14250 ± 236.2
Y-intercept (X=0.0)	12.10 ± 1160	-104.2 ± 278.3	-81.16 ± 166.2	-185.4 ± 444.3
X-intercept (Y=0.0)	-0.0003748	0.01196	0.01465	0.01301
1/slope	0.00003097	0.0001148	0.0001805	0.00007018
r^2	0.9985	0.9988	0.9990	0.9989
95% Confidence Intervals:				
Slope	30580 to 34010	8299 to 9120	5294 to 5785	13590 to 14900
Y-intercept (X=0.0)	-3209 to 3233	-876.9 to 668.5	-542.5 to 380.1	-1419 to 1048
X-intercept (Y=0.0)	-0.1028 to 0.09704	-0.07856 to 0.09858	-0.07014 to 0.09600	-0.07525 to 0.09755

Repeatability

Seven repeat injections (separated by a blank sample) of a diluted reference solution (1/10000) were performed. Water used in dilutions was charcoal filtered (R > 18 MΩ). [NDELA(aq)] = 228×10^{-9} g/g (228 ppb). Repeatability data are contained in Table 4.4 for each of the transitions monitored. Total NO loss is the sum of the transitions 135 → 104 and 135 → 105.

Table 4.4. Repeatability data for injections of NDELA, [NDELA(aq)] = 228 ppb.

	Peak Area (Ion counts) [NDELA] = 228 ppb			
	135 → 74	**135 → 104**	**135 → 105**	**Total NO loss**
	4845	1203	631	1834
	4757	1123	1122	2245
	4559	1276	634	1910
	5089	1346	932	2278
	5491	1451	889	2340
	4388	1280	866	2146
	4566	1425	987	2412
Mean	4814	1301	866	2166
σ_{Mean}	1819.5	491.7	327.3	818.7
1.96σ_{Mean}	3566	964	642	1605
95 % +	8380	2265	1508	3771
95 % -	1248	337	225	561
[NDELA] 95 % C.I., ppb	38-259	51-272	55-287	52-278
1.64σ_{Mean}	2984	806	537	1343
90 % +	7798	2107	1403	3509
90 % -	1830	495	329	823
[NDELA] 90 % C.I., ppb	56-241	69-254	74-268	71-259
S.D.	376	117	180	218
S.D./Mean × 100	7.8	9.0	20.8	10.1

Discarding one outlier point for each transition, the following graphs presented in Figure 4.1. were derived for six injections.

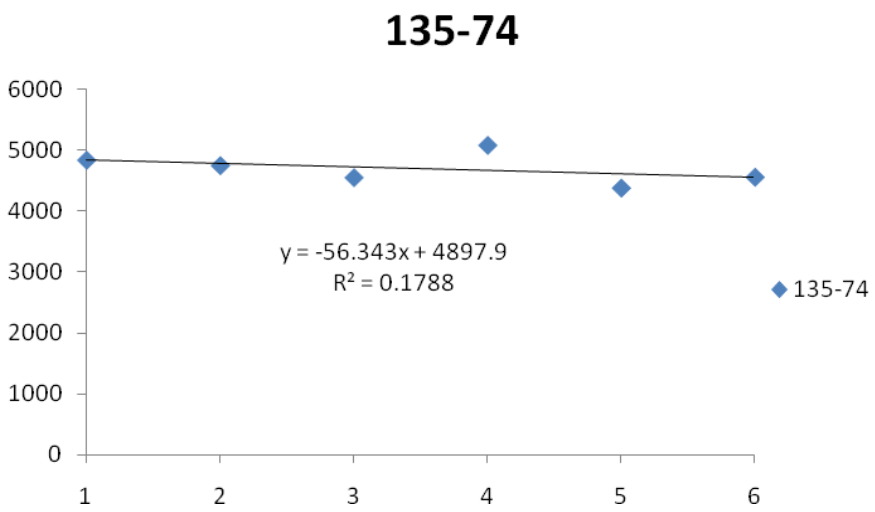
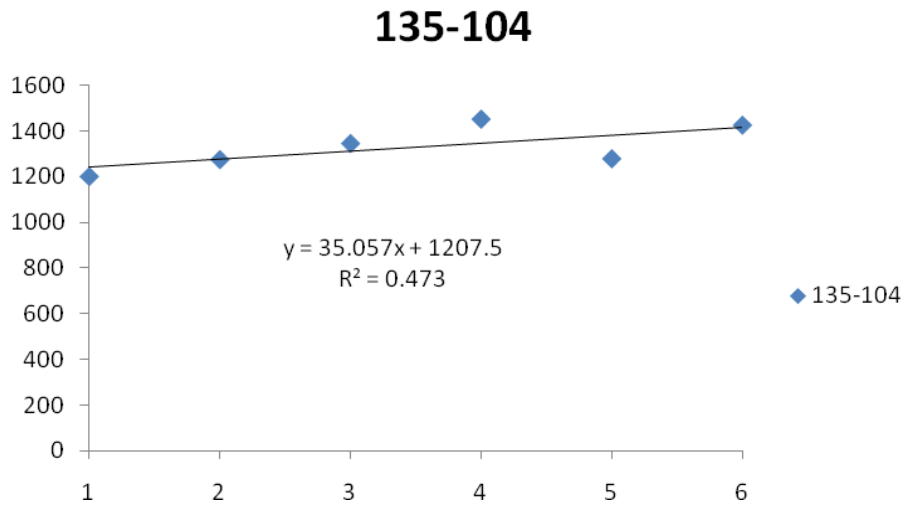
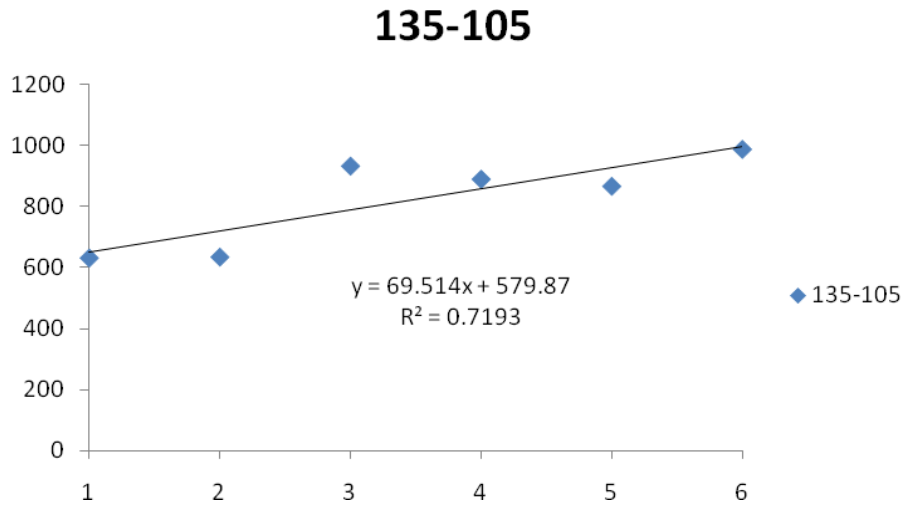


Figure 4.1. Reproducibility of consecutive injections of NDELA in charcoal filtered water, [NDELA] =228 ppb. Y-axis: peak area, X-axis: injection number. Transition 135 → 74.





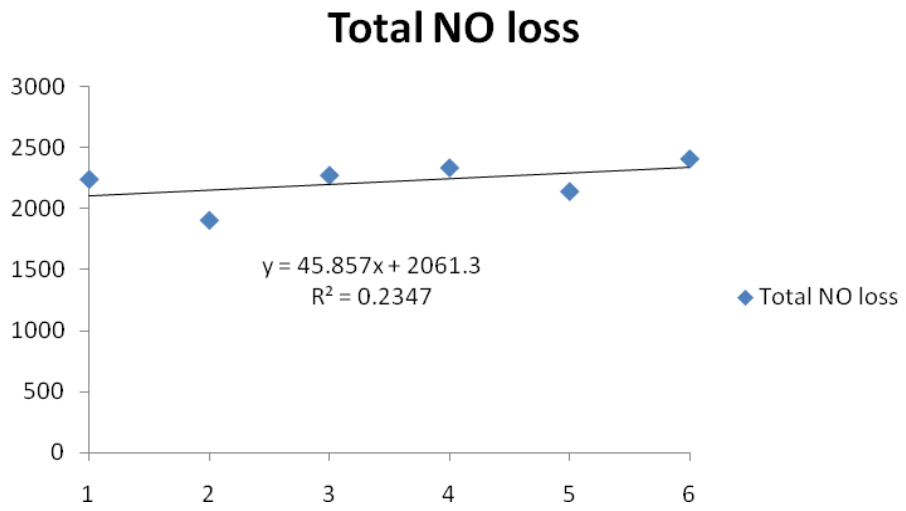


Figure 4.1. continued Repeatability of consecutive injections of NDELA in charcoal filtered water, [NDELA] =228 ppb. Y-axis: peak area, X-axis: injection number. Transitions 135 → 104, 135 → 105, total NO loss.

The standard deviation, as a percentage of the mean of six replicates, for each of the transitions is as follows: 135 → 74, 5.3 %; 135 → 104, 7.1 %; 135 → 105, 18.6 %; total NO loss, 8.0 %.

Matrix effects

Loaded MEA solution (30 % w/w, 300 mg MEA/ml H_2O, loading 0.54 mol CO_2/mol amine) and various salts (1 mg salt/ml H_2O) commonly detected in PCC liquors were investigated for their effects on the analyte signal under the conditions specified in "Experimental conditions for standardisation of NDELA in an aqueous matrix" section. Formate and acetate were not investigated (formate is present in the mobile phase, and acetate is the next congener in the homologous series of carboxylate ions).

Sample preparation: 20 mg (to the nearest mg) of the following salts were weighed and charcoal filtered water added until the final mass was 10.000 g (to the nearest milligram): KNO_3, Na_2SO_4, $H_2C_2O_4$, $NaHCO_3$. 1 ml of this solution together with 20 μl of reference solution diluted by a factor of 1/100 were added to 980 μl of charcoal-filtered water. Final solution concentrations were 1000 ppm salt, 0.23 ppm NDELA. Peak area results for these samples (plus repeat injections of an NDELA solution in charcoal-filtered water, [NDELA] = 0.23 ppm) are presented in Table 4.5. All analyte responses in the presence of matrix fall within the 90 % confidence limit. There is limited – if any – signal suppression. A small aliquot of 30 % w/w MEA (20 μl, 3 mg, 1.5 mg/ml) appears to slightly enhance the detector response.

Table 4.5. Replicate NDELA runs and the effect of various salts and a small aliquot of 30 % w/w MEA on the NDELA signal at 228 ppb.

	Peak Area (ion counts) [NDELA] = 228 ppb			
	135 → 74	**135 → 104**	**135 → 105**	**Total NO loss**
[NDELA] = 228 ppb	4845	1203	631	1834
	4757	1123	1122	2245
	4559	1276	634	1910
	5089	1346	932	2278
	5491	1451	889	2340
	4388	1280	866	2146
	4566	1425	987	2412
Mean	4814	1301	866	2166
σ_{Mean}	1819.5	491.7	327.3	818.7
[NDELA], 228 ppb + 1mg/ml salt, salt =				
KNO_3	4582	1354	960	2314
Na_2SO_4	5571	1789	991	2780
$H_2C_2O_4$	4143	1007	649	1656
$NaHCO_3$	4345	1425	838	2263
20 μl 30 % w/w MEA + 228 ppb NDELA	6865	2237	1455	3692

Blind spiking trial/recovery test

Test samples: 10 test samples, 2 ml total volume containing 30 % w/w, 300 mg MEA/ml H_2O, loading 0.54 mol CO_2/mol amine, were prepared. Before sub-sampling, two of the test samples were spiked with NDELA reference solution; one to a final concentration of ~ 2.0 ppm, and a separate solution to a final concentration of ~ 0.2 ppm.

1. Test portions: 200 μl of each unknown was added to 1800 μl charcoal-filtered water (total volume 2 ml). The final concentrations of [NDELA] in the portions subjected to IC-MRM analysis was 200 ppb (2 ppm spike) and 20 ppb (0.2 ppm spike). The IC-MRM transitions for unknown test sample 4 are presented in Figure A4.2.

Significant matrix effects reduce the overall detector response to NDELA, and this is particularly evident in the transition 135 $\rightarrow$ 74. It can be seen in this transition that the majority of the salt/MEA in the sample elutes at t_R = 8-11 mins. The presence of peaks at t_R = 4.00 in each of the primary transitions being monitored confirms the presence of NDELA in test sample 4 (see Figure A4.2.). There was no indication of NDELA in any of the other test samples, confirming that test sample 4 contained the higher NDELA concentration (2.0 ppm). Direct analysis of test portions with [NDELA] $\leq$ 0.2 ppm containing 30 mg/ml MEA is useful only for screening purposes.

2. Internal standard: 200 μl of each test sample was added to 1780 μl charcoal-filtered water and 20 μl of diluted reference solution (factor of 100), total test portion volume 2 ml. For test portion 4, [NDELA] = 2.2 ppm, [MEA] = 30 mg/ml.

Signal suppression proved to be problematic again. All samples exhibited chromatographic peaks at t_R = 4.0 mins, which confirmed the presence of NDELA, however the peak shapes were very poor (typically spikey, a common peak shape characteristic when ion-pairing in the source is occuring). This is due to the high MEA concentration in the test portion. Quantitation of NDELA in the presence of 30 mg/ml MEA is not feasible using IC-MRM.

3. Internal standard: 100 μl of each test sample was added to 1880 μl charcoal-filtered water and 20 μl of diluted reference solution (1/100), total test portion volume 2 ml, [MEA] = 15 mg/ml. Duplicate analyses were performed. The mean duplicate results are presented graphically in Figure 4.3.

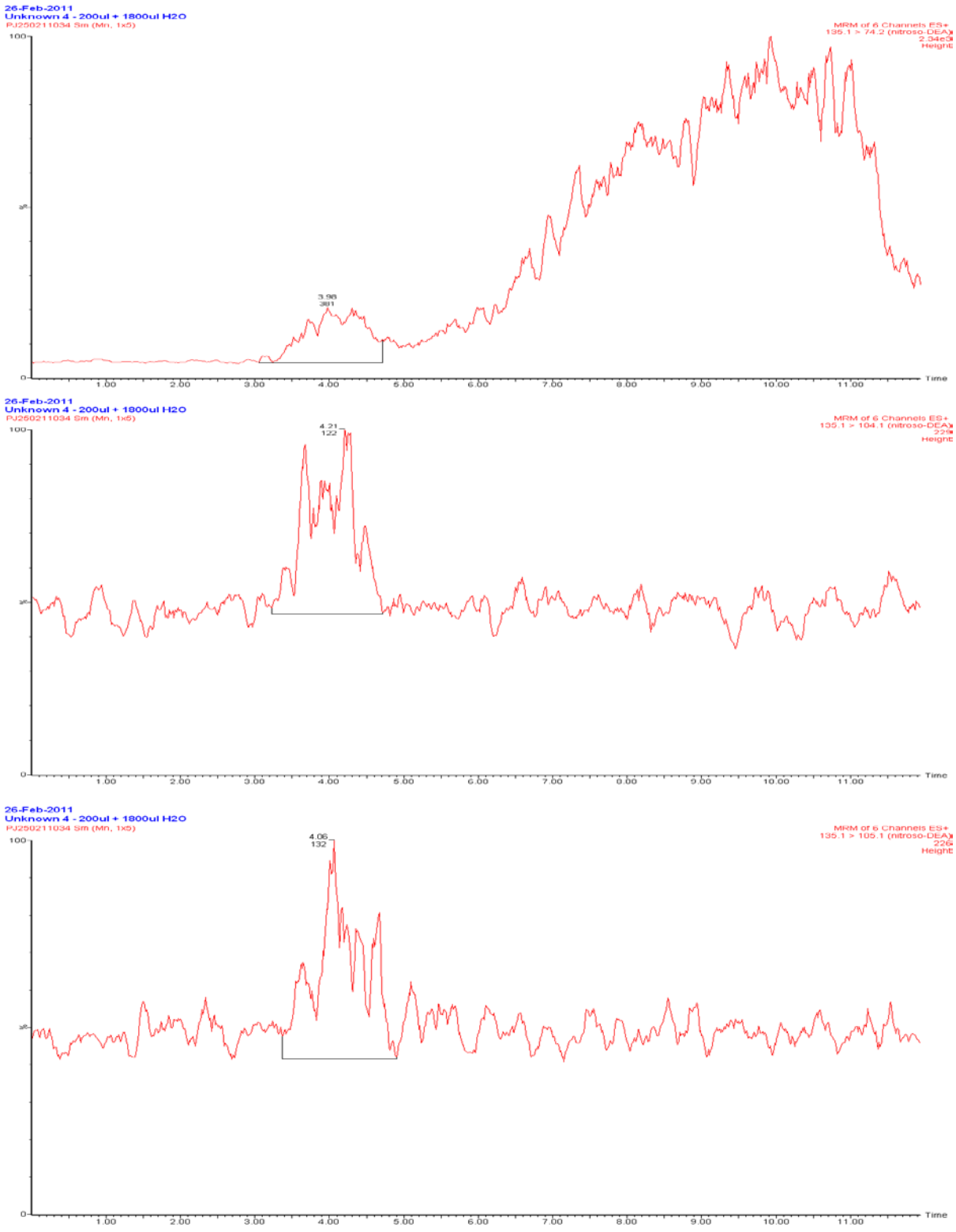


Figure 4.2. Chromatographic peaks for NDELA (0.23 ppm) in the presence of 30 mg/ml MEA. Top: 135 → 74; Centre: 135 → 104; Bottom: 135 → 105.

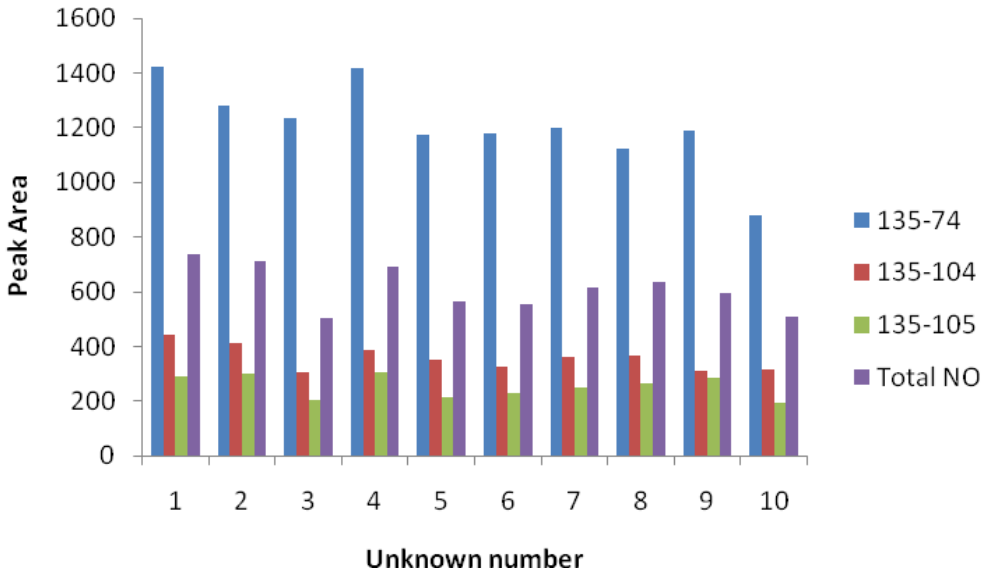


Figure 4.3. Peak areas for each of the transitions monitored, and the results for total NO loss.

On the basis of this graph, and the screening study, unknown test portion 4 contains NDELA. Test portions 1 or 2 possibly contain a smaller amount of NDELA. Consultation with the technician who prepared the samples confirmed Unknown 4 was spiked with 2 ppm NDELA. Unknown sample 7 was spiked with 0.2 ppm NDELA.

Calibration curves for samples containing 7.5 mg/ml MEA.
For the purposes of analysing samples containing a range of MEA concentrations, calibration standards were prepared by adding 50 μl of 30 % w/w 0.54 loaded MEA (15 mg MEA) to 1930 μl charcoal-filtered water. 20 μl additions of diluted reference solution (charcoal-filtered water) were added, [$MEA_{(aq)}$] = 7.5 mg/ml. The regression data for the averages of the triplicate analyses at each concentration are presented in Table 4.6., together with instrument LOD and LOQ values for each of the transitions.

A series of unknown test solutions have been analysed for CCM as part of the call-off work. In the first analysis, 50 μl of each unknown was added to 1950 μl charcoal-filtered water and subjected to analysis (direct analysis). CCM ID=A and CCM ID=M samples were found to contain significant amounts of NDELA. The results for duplicate analyses of these two samples are presented in Table 4.7. In a separate experiment, the test solutions were diluted as described for the direct analysis, and then spiked with 229 ppb NDELA. The results for this analysis are presented in Table 4.8.

Table 4.6. Standard regression results for a serial dilution of the reference solution in charcoal-filtered water, [loaded MEA] = 7.5 mg/ml.

	135 → 74	**135 → 104**	**135 → 105**	**Total NO loss**
Slope	6489 ± 106.3	1720 ± 60.88	1149 ± 44.70	2869 ± 105.6
Y-intercept (X=0.0)	97.27 ± 206.8	106.7 ± 118.4	76.85 ± 86.94	183.6 ± 205.3
X-intercept (Y=0.0)	-0.01499	-0.06205	-0.06690	-0.06399
1/slope	0.0001541	0.0005813	0.0008705	0.0003486
r^2	0.9987	0.9938	0.9925	0.9933
95% Confidence Intervals:				
Slope	6216 to 6762	1564 to 1877	1034 to 1264	2598 to 3140
Y-intercept (X=0.0)	-434.3 to 628.8	-197.7 to 411.2	-146.7 to 300.4	-344.3 to 711.5
X-intercept (Y=0.0)	-0.09932 to 0.06542	-0.2529 to 0.1095	-0.2783 to 0.1212	-0.2630 to 0.1142
Instrument LOD (peak area)	300	203	205	372
Instrument LOQ (peak area)	444	272	277	477
Instrument LOD (ppb)	**31**	**56**	**112**	**66**
Instrument LOQ (ppb)	**53**	**96**	**174**	**102**
Method LOD (ppb)	**1240**	**2240**	**4480**	**2640**
Method LOQ (ppb)	**2120**	**3840**	**6960**	**4080**

Table 4.7. Results for CCM ID=A and CCM ID=M unknown samples. Direct injection of dilute test sample, dilution factor = 1/40.

	Peak Area (Ion counts) [NDELA]			
	135 → 74	**135 → 104**	**135 → 105**	**Total NO loss**
CCM ID=A	6661	1617	1083	2700
	5062	1567	814	2381
Mean	5862	1592	949	2541
Instrument [NDELA], ppb	888	863	759	822
Method [NDELA], ppm	35.5	34.5	30.4	32.9
CCM ID=A, [NDELA] =	33.3 ± 2 ppm			
CCM ID=M	5815	1217	929	2146
	6138	1551	955	2506
Mean	5977	1384	942	2326
Instrument [NDELA], ppb	906	743	753	747
Method [NDELA], ppm	36.2	29.7	30.1	29.9
CCM ID=M, [NDELA] =	31.5 ± 3 ppm			

Table 4.8. Results for CCM ID=A and CCM ID=M unknown samples. Direct injection of spiked test samples (229 ppb), dilution factor = 1/40.

	Peak Area (Ion counts) [NDELA]			
	135 → 74	**135 → 104**	**135 → 105**	**Total NO loss**
CCM ID=A	6177	1732	1110	2842
Instrument [NDELA]-spike, ppb	708	716	670	698
Method [NDELA], ppm	28.3	28.6	26.8	27.9
CCM ID=A, [NDELA] =	27.9 ± 0.8 ppm			
CCM ID=M	6555	2029	1380	3409
Instrument [NDELA]-spike, ppb	766	888	905	895
Method [NDELA], ppm	30.6	35.5	36.2	35.8
CCM ID=M, [NDELA] =	34.5 ± 2.6 ppm			

Four other samples are suspected to contain NDELA. Small peaks were observed in various transitions that were close to, or less than, the LOD of the method. These samples were ID=E, ID=I, ID=P and ID=J. The results are reported for the apparent concentration of NDELA in Table 4.9. At or near the detection limit, false positives are highly probable and the results are useful for screening only.

Table 4.9. Results for unknown samples at, or below, the instrument LOD. Direct injection of test samples.

	Peak Area (Ion counts) [NDELA]			
	135 → 74	**135 → 104**	**135 → 105**	**Total NO loss**
CCM ID=E	404	150	118	268
Instrument [NDELA], ppb	47	25	36	29
Method [NDELA], ppm	4.7	2.5	3.6	2.9
CCM ID=E, [NDELA] =	3.4 ppm			
CCM ID=I	210	153	67	220
Instrument [NDELA], ppb	17	27	0.0	13
Method [NDELA], ppm	1.7	2.7	0	1.3
CCM ID=I, [NDELA] =	1.4 ppm			
CCM ID=J	204	193	94	287
Instrument [NDELA], ppb	16	50	15	36
Method [NDELA], ppm	1.6	5.0	1.5	3.6
CCM ID=J, [NDELA] =	2.9 ppm			
CCM ID=P	286	156	120	276
Instrument [NDELA], ppb	29	29	38	32
Method [NDELA], ppm	2.9	2.9	3.8	3.2
CCM ID=P, [NDELA] =	3.2 ppm			

Comments/Summary

The LOD's/LOQ's would be lowered significantly if a method for separation of the the analyte (NDELA) from the matrix (30 % w/w MEA) could be established. The reported values for the method are largely determined by the trade-off between (tolerable) signal suppression and sample dilution. Utilising ion chromatography achieves an acceptable analyte:matrix separation, but there is room for improvement. For 30 % w/w MEA, screening is feasible with a dilution of 1/10-1/20 (if quantitation can be sacrificed). In order to avoid signal suppression in the electrospray ion source, the concentration of MEA in the test solution should be < 10 mg/ml. Obtaining a satisfactory reference material (of known purity) would also enhance the results. The transition 135 → 74 is the most sensitive and should be used for empirical LOD determinations.

References

Jackson, P.; Attalla, M.I. (2010) N-Nitrosopiperazines form at high pH in post-combustion capture solutions containing piperazine: a low-energy collisional behaviour study. *Rapid Commun. Mass Spectrom.* 24: 3567–3577.

Schothorst, R.C.; Somers, H.H.J. (2005) Determination of N-nitrosodiethanolamine in cosmetic products by LC-MS-MS. *Anal. Bioanal. Chem.* 381: 681-685.

Appendix (Section 4)

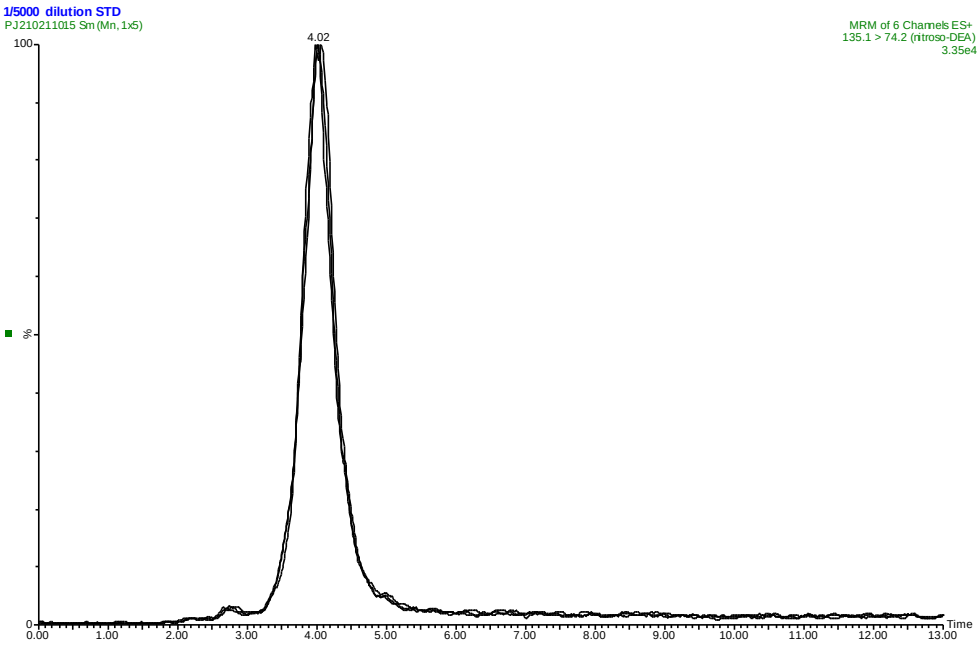


Figure 4.4. Repeatability of injections (NDELA reference solution, dilution factor = 1/5000, [NDELA] = 458 ng/ml, five injections, one injection per hour separated by 2 blank runs). Overlay of m/z 135-74 transition for peak areas, retention times.

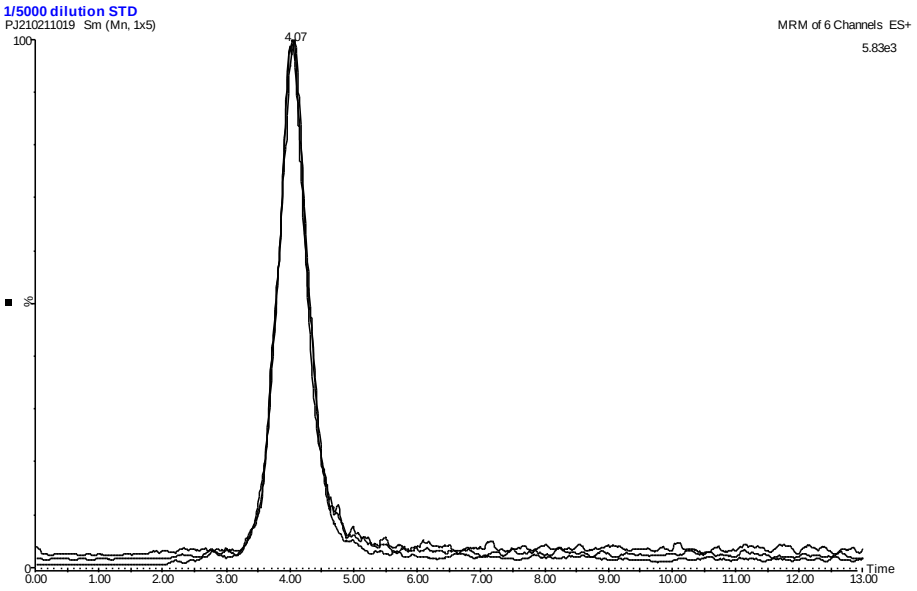


Figure 4.5. Overlay of all three transitions being monitored (NDELA reference solution, dilution factor = 1/5000, [NDELA] = 458 ng/ml, one injection).

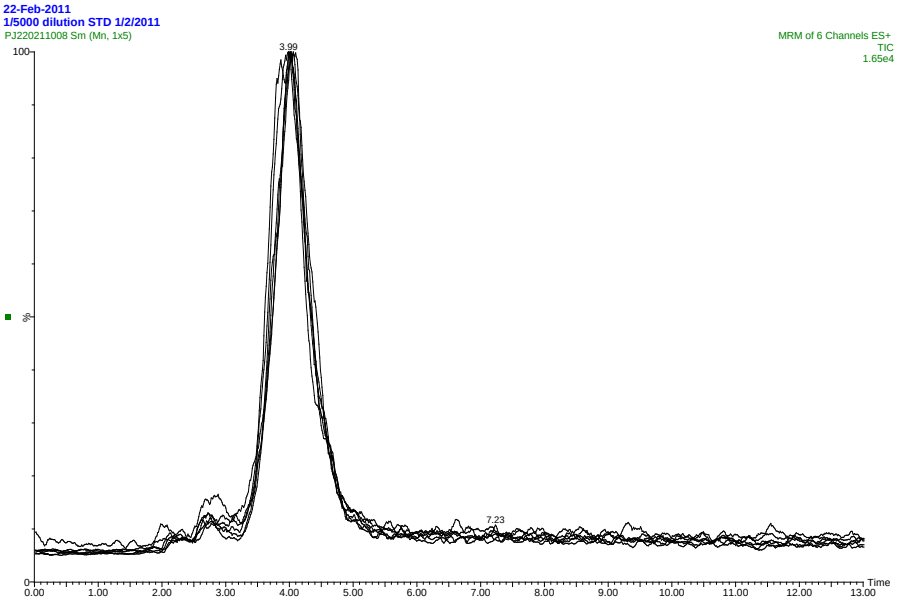


Figure 4.6. Overlay of mass chromatograms of dilute NDELA reference solution (factor = 1/5000), in a matrix of water only (3 chromatograms) and a matrix of water + 3 mg/ml MEA.

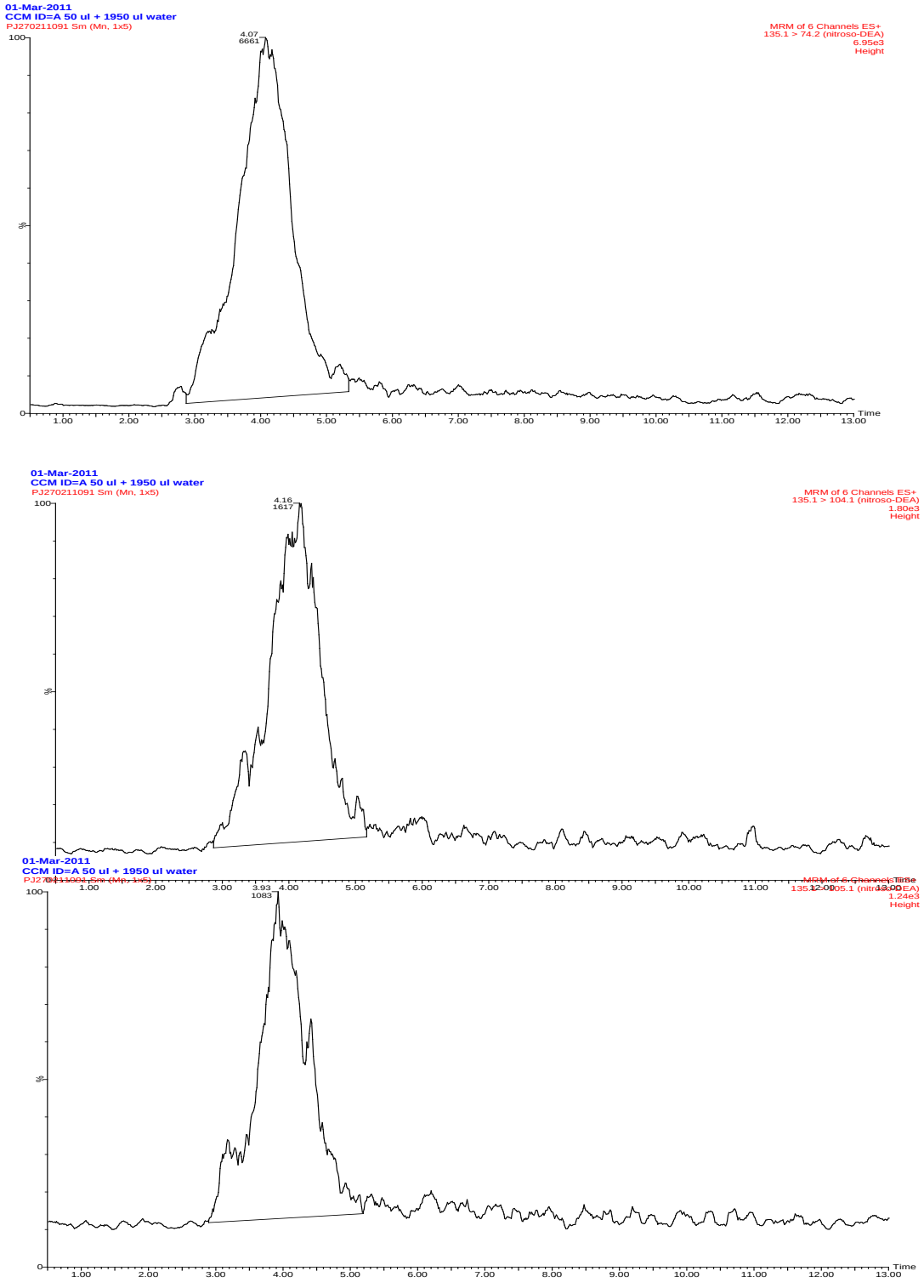


Figure 4.7. Mass chromatograms for unknown sample CCM ID=A. Top: 135 → 74. Centre: 135 → 104. Bottom: 135 → 105

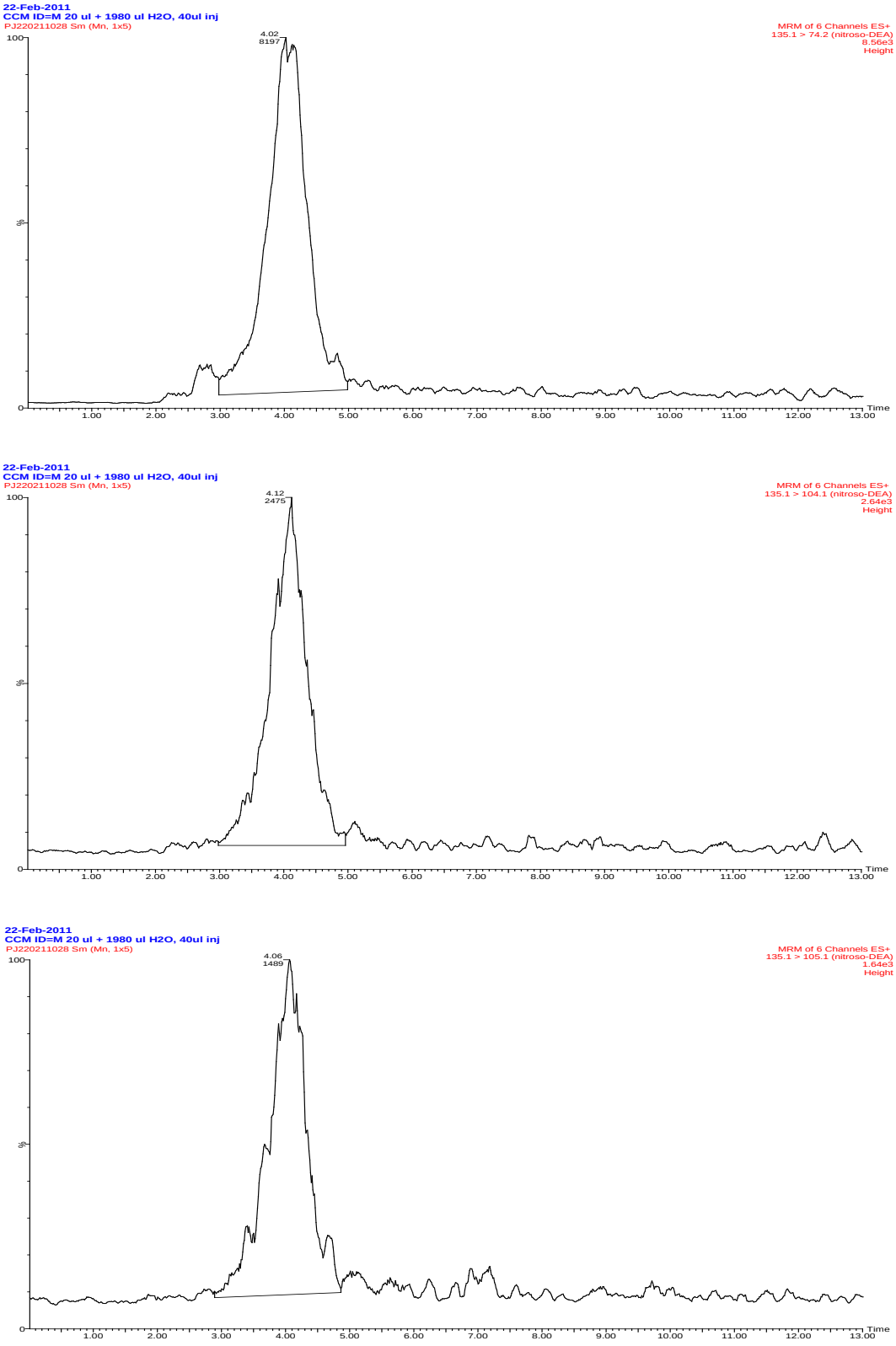


Figure 4.7. continued Mass chromatograms for unknown sample CCM ID=M. Top: 135 → 74. Centre: 135 → 104. Bottom: 135 → 105.

5. QUANTITATIVE METHOD FOR N-NITROSOPIPERAZINE (NPZ) IN AQUEOUS SOLUTIONS

A shortened, precise version of this method is given in Appendix 2 (i.e. without any of the "work-up data included).

Title. Quantitative method for N-nitrosopiperazine (NPZ) in aqueous solutions using reversed-phase HPLC-MS/MS

Authors. CSIRO (specifically, P. Jackson and M.I. Attalla)

Introduction. This method utilises reverse phase HPLC in combination with an MS detector for the measurement and detection of N-nitrosopiperazine. The MS analysis mode employed is multiple reaction monitoring (MRM). In total, three dissociative transitions are monitored at a common retention time (t_R) for analyte identification, and where possible, all three are used for quantitation. At low analyte concentrations, M/z 116 $\rightarrow$ 85 and M/z 116 $\rightarrow$ 86 transitions afford the best opportunities for quantitation, as they are "metastable-like" in their energy demand, in contrast to M/z 116 $\rightarrow$ 44 which requires significant precursor bond-breaking/rearrangement.

Jackson and Attalla (2010) have demonstrated that the two major transitions which describe the loss of the nitroso-functional group in N-nitrosopiperazine (loss of NO, 30 Da, and loss of HNO, 31 Da) occur at almost the same energy demand. As a result, the abundance of the product ions (M/z 85, M/z 86) varies unpredictably over a small collision energy range that might typically be used in tandem mass spectrometry experiments. Monitoring a single transition may not be suitable for quantitation purposes. For this reason both losses of NO and HNO are monitored (as a sum to represent total loss of the NO functional group). This also eliminates any uncertainty that could arise from instrument cross-talk. Cross-talk is problematic in low-resolution tandem mass spectrometry instruments when the DC:RF ratio is relaxed (lower DC) to maximise sensitivity. When two transitions are separated by less than 1 M/z unit, this situation can be exacerbated.
Unlike ion chromatography, analyte pH can shift reverse phase retention times if the mobile phases have limited buffering capacity. Buffer systems cause in-source ion pairing in the MS detector (compromising sensitivity) and should be avoided where possible, even to the point of mild deterioration of the chromatographic peak shape. Post-combustion capture solutions typically possess pH's > 8, so retention time cannot be considered a water-tight analyte identification parameter.

Warning. *N-nitrosopiperazine (NPZ, CAS 5632-47-3) is a potential carcinogen and appropriate precautions (e.g wearing appropriate PPE, sample manipulations in a certified fumehood) should be exercised when handling the reference material, any reference solution or PCC liquors.*

Scope.
Definitions of limit-of-detection (LOD) and limit-of-quantitation (LOQ), as described in the ISO normative reference 2, are too prescriptive for application to trace detection using sophisticated instrumental methods; see normative reference 3 (N3). In this article (N3), two approaches to determining LOD are described: a statistical method (mean + 3 $\times$ S.D., number of blank samples = 6) and an empirical method. The empirical method entails serial dilution of the reference standard; increasingly dilute reference samples are then analysed until the measurable (associated with the analyte) is no longer distinguishable from the baseline. In water, a LOD of approximately 2 ng/ml (ppb) is obtained empirically using the M/z 116 $\rightarrow$ 85 transition. The results obtained using statistical methods for NPZ in water are

presented in Table 5.1. The statistical LOQ is defined as the mean + 6 × S.D.'s (number of blank samples = 6).

Table 5.1. Statistical LOD/LOQ for NPZ in water using HPLC-MS/MS.

Transition	LOD		LOQ	
	Peak area	**[NPZ], ppb**	**Peak area**	**[NPZ], ppb**
116 → 44	668	**12**	1034	**34**
116 → 85	263	**2.4**	392	**3.5**
116 → 86	282	**5.6**	426	**8.5**
Total NO loss	464	**2.8**	656	**3.9**

Due to the presence of an underivatized secondary nitrogen centre in NPz, ion-pairing with matrix components is problematical during analyte measurement. It also renders separation of the analyte from the matrix almost impossible using wet-chemical or chromatographic techniques. At a concentration of 4.84 ppm NPz and 120 ppm loaded Pz, 99 % of the signal is suppressed. If the LOD in water (Table 5.1.) represents the signal measured when there is 99 % suppression by loaded Pz, an estimate of the detection limit pertaining to NPz in loaded solutions can be determined for each transition (assuming the suppression effect is linear with [NPz]). For M/z 116 → 44, LOD = 5.1 ppm; M/z 116 → 85, LOD = 0.26 ppm; M/z 116 → 86, LOD = 0.60 ppm.

The values in Table 5.1 and the equations presented in Figure 5, Section B10.3, can also be used to estimate the maximum tolerable concentration of loaded Pz which can be present with NPz before complete signal suppression. For M/z 116 → 44, [Pz] = 112 ppm; M/z 116 → 85, [Pz] = 213 ppm; M/z 116 → 86, [Pz] = 174 ppm. These values assume [Pz] is not limiting. Due to the strong ion-pairing nature of the analyte, it is recommended that this method is only applied to wash- and discharge waters when [Pz] < 150 ppm (for detection only), preferably when [Pz] < 100 ppm.

Normative references and bibliography.

Chemistry – Layouts for standards – Part 2. Methods of chemical analysis. International Standards Organisation document ISO 78-2:1999(E).

Accuracy (trueness and precision) of measurement methods and results – Part 1: General principles and definitions. International Standards Organisation document ISO 5725-1:1994(E).

Armbruster, D.A.; Tillman, M.D.; Hubbs, L.M. (1994) Limit of detection (LOD)/Limit of quantitation (LOQ): Comparison of the empirical and statistical methods exemplified with GC-MS Assays of abused drugs. Clin. Chem. 40: 1233-1238.

General requirements for the competence of testing and calibration laboratories. International Standards Organisation document ISO 17025:2005(E).

Definitions.

NPZ *N-nitrosopiperazine*

PZ	*Piperazine*
MRM	*multiple reaction monitoring*
HPLC	*high performance liquid chromatography*
PCC	*post combustion capture*
MS	*mass spectrometer*
t_R	*chromatographic retention time*
Transition	*reproducible fragmentation or dissociation of mass-selected analyte [M+H]+ induced by collision with an inert gaseous target under specified conditions*
DC:RF	*ratio of direct current (DC, resolving) selectively superimposed on radio-frequency (RF) current and applied to quadrupole rods to control the stability of certain ion orbits (with selected M/z ratio) within the quadrupole, such that the ion motion satisfies the Mathieu equations*
LOD	*limit of detection*
LOQ	*limit of quantitation*
σ_M	*mean/$(N)^{1/2}$, where N = number of measurements or samples, or sample size*
S.D.	*standard deviation*
C.I.	*confidence interval*

Reagents

Water, CAS 7732-18-5, purified to compliance with ASTM (D1193-91) Type 1*, R > 18 MΩ/cm
Formic acid, CAS 64-18-6, > 99 %
Methanol, CAS 67-56-1, HPLC grade
2-aminoethanol (MEA), CAS 9007-33-4, > 99 %
Oxalic acid, CAS 144-62-7, > 99 %
Potassium nitrate, CAS 7757-79-1, > 99.0 %
Sodium sulphate anhydrous, CAS 7757-82-6, > 99 %
Sodium bicarbonate, CAS 144-55-8, > 99.5 %

Experimental conditions for standardisation of NPZ in an aqueous matrix.

Test sample injection volume: 40 µl
Instrumentation: LC-MS/MS (Waters Acquity MS^2)
Ion mode: Positive ion electrospray
MS operation mode: multiple reaction monitoring (MRM)
Capillary voltage: 3.57 kV
Cone voltage: 20 V
Extractor: 2.0 V
RF: 0.2 V
Source temperature: 150 °C
Desolvation temperature: 350 °C
Desolvation gas flow rate: 500 L/hr
Collision gas flow rate: 0.03 ml/min
Transition dwell time: 0.1 s
Interscan delay: 0.02 s
Inter-channel delay: 0.02 s
MS1 low mass resolution: 14.0
MS1 high mass resolution: 14.0
MS3 low mass resolution: 13.5
MS3 high mass resolution: 13.5
MS analyser baseline pressure: $< 1.3 \times 10^{-5}$ mbar
MS analyser pressure after admission of collision gas: $1.2\text{-}1.3 \times 10^{-3}$ mbar
Collision gas: high purity argon
T-cell bias: 12 V

Multiplier voltage: -645 V
Run time: 25 mins
Transitions:
(i) 116.1 $\rightarrow$ 44.1
(ii) 116.1 $\rightarrow$ 86.1
(iii) 116.1 $\rightarrow$ 85.1
Peak height or peak area used: Peak area
Smoothing prior to peak integration: Mean of 5 scans
Column: C18, 3.5 μm x (2.1 x 100) mm
Column temperature: 20 °C
Injection volume: 40 μl
Mobile phases: A = 100 % MeOH (LC-MS grade, Sigma Aldrich), B = charcoal-filtered water
Gradient:

Table 5.2. HPLC-MS/MS gradient conditions

Time (mins)	A %	B %	Flow rate (ml/min)
0.00	50.0	50.0	0.500
8.00	50.0	50.0	0.500
15.00	98.0	2.0	0.500
16.00	98.0	2.0	1.000
18.50	98.0	2.0	1.000
19.00	2.0	98.0	1.000
21.50	2.0	98.0	1.000
22.00	50.0	50.0	0.500

NPZ standard material: purchased from Toronto Research Chemicals (Canada), purity not specified (assumed > 90 %. Major contaminants: N,N′-dinitrosopiperazine.
Standard NPZ solution = 24.2×10^{-3} g NPZ added to 10 ml charcoal-filtered water (R > 18 MΩ). [NPZ] = 2.4 $\pm$ 0.2 milligrams/millilitre.
Total solution mass = 10.0242 g
This solution was used to evaluate the performance of NPZ quantification in all matrices. Hereafter it is referred to as the reference solution.
t_R (NPZ) $\cong$ 3.0 mins.

Calculations

Linearity

Curve-fit regression results for a series of dilutions of the reference solution in charcoal-filtered water are presented in Table 5.3. Note that the best fits to the data are obtained using second order polynomials for each transition when the concentration range spans four orders of magnitude. [$NPZ_{(aq)}$] = 4.84×10^{-9} g/ml, 24.2×10^{-9} g/ml, 48.4×10^{-9} g/ml, 242×10^{-9} g/ml, 484×10^{-9} g/ml, 2.42×10^{-6} g/ml, 4.84×10^{-6} g/ml.

Table 5.3. Standard regression results for a serial dilution of the reference solution in charcoal-filtered water.

Area = A + B*[NPz] + C*[NPz]^2	116 → 86	116 → 85	116 → 44	Total NO loss
A	1162	1778	470.1	3266
B	53491	88256	16680	141429
C	-3071	-5804	-809.7	-8822
Std Errors:				
A	820.0	1167	268.0	2165
B	1642	2510	536.7	4335
C	349.4	538.3	114.2	922.5
r²	0.9995	0.9994	0.9995	0.9995
95% Confidence Intervals:				
A	-945.9 to 3271	-1078 to 4633	-218.9 to 1159	-2299 to 8832
B	49269 to 57713	82114 to 94398	15300 to 18060	130284 to 152575
C	-3969 to -2173	-7121 to -4487	-1103 to -516.1	-11190 to -6451

Repeatability

Seven repeat injections (separated by a blank sample) of a diluted reference solution (1/10000) were performed. Water used in dilutions was charcoal filtered (R > 18 MΩ). [NPz(aq)] = 242 × 10^{-9} g/g (242 ppb). Repeatability data are contained in Table 5.4 for each of the transitions monitored. Total NO loss is the sum of the transitions 116 → 85 and 116 → 86. Discarding one outlier point for each transition, the following graphs presented in Figure A5.1. were derived for six injections.

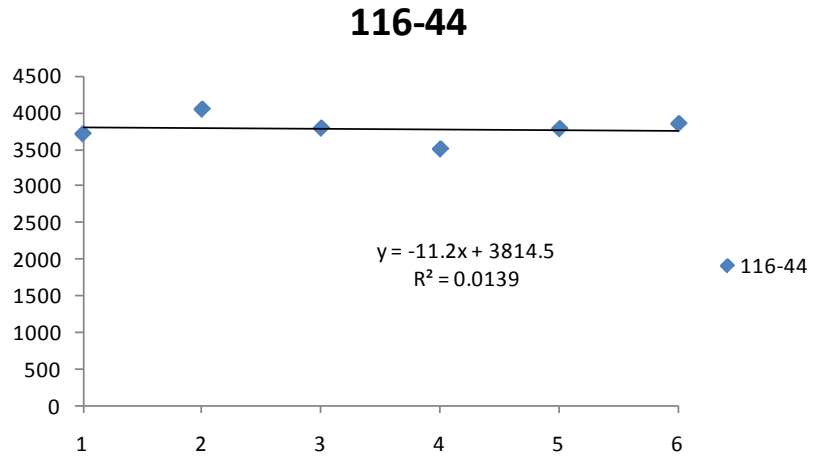


Figure 5.1. Repeatability of consecutive injections of NPz in charcoal filtered water, [NPz] = 242 ppb. Y-axis: peak area, X-axis: injection number. Transition 116 → 44.

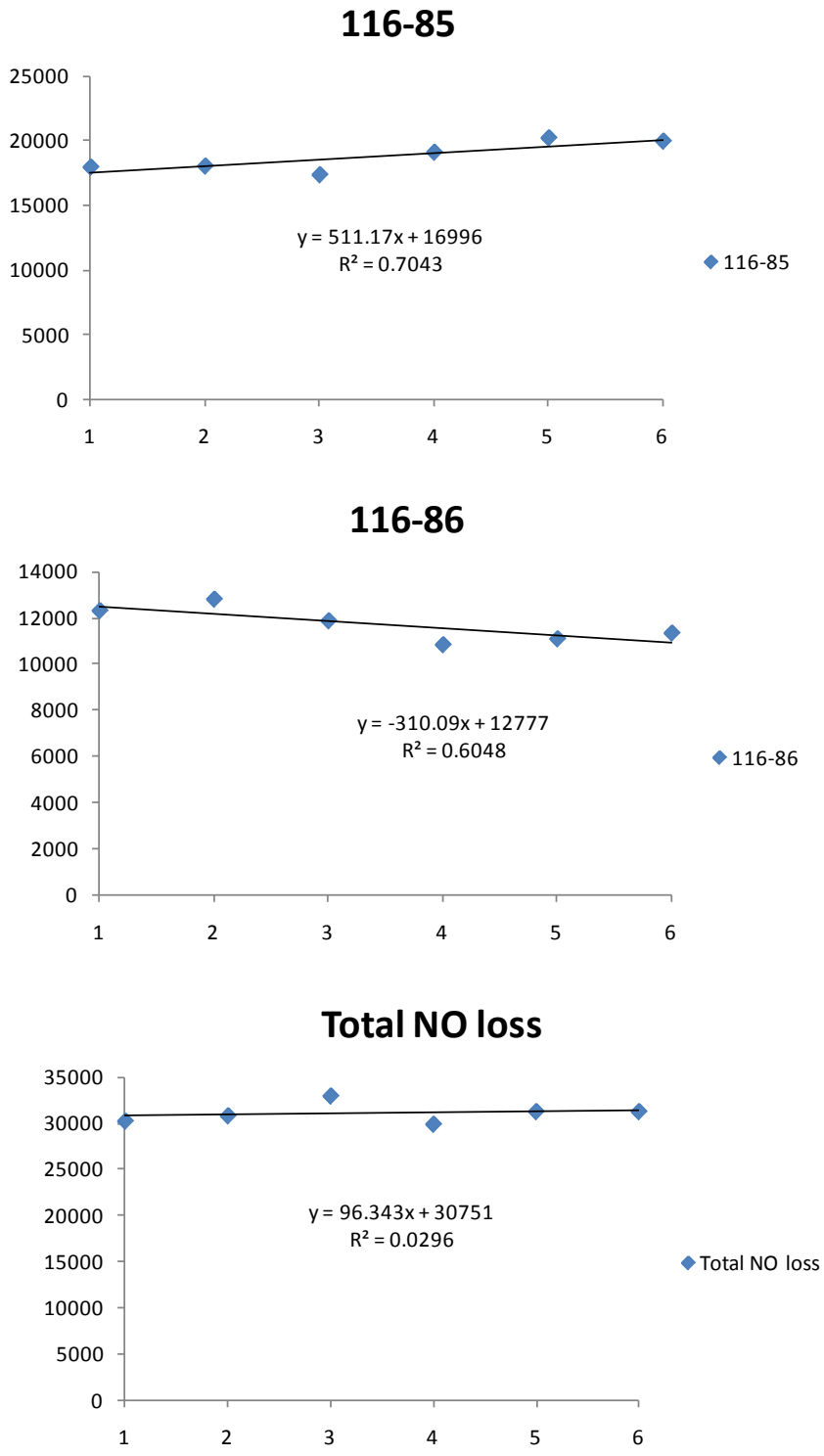


Figure 5.1. continued Repeatability of consecutive injections of NPz in charcoal filtered water, [NPz] = 242 ppb. Y-axis: peak area, X-axis: injection number. Transitions 116 → 85, 116 → 86, total NO loss.

Table 5.4. Repeatability data for repeat injections of aqueous NPz, [NPz(aq)] = 242 ppb.

	Peak Area (Ion counts) [NPz] = 242 ppb			
	116 → 44	**116→ 85**	**116 → 86**	**Total NO loss**
	3706	17987	12283	30270
	4043	18065	12772	30837
	3784	17409	10567	27976
	4431	21075	11851	32926
	3498	19110	10832	29942
	3776	20195	11084	31279
	3845	19947	11329	31276
Mean	3869	19113	11531	30644
σ_{Mean}	1462	7224	4358	11582
1.96σ_{Mean}	2866	14159	8542	22701
95 % +	6735	33272	20073	53345
95 % -	1003	4954	2989	7943
[NPz] 95 % C.I., ppb	32-383	36-366	34-361	33-362
1.64σ_{Mean}	2398	11847	7148	18995
90 % +	6267	30960	18679	49639
90 % -	1471	7266	4383	11649
[NPz] 90 % C.I., ppb	60-354	62-338	60-334	60-335
S.D.	296	1353	803	1516
S.D./Mean × 100	7.7	7.1	7.0	4.9

The standard deviation, as a percentage of the mean of six replicates, for each of the transitions is as follows: 116 → 44, 4.7 %; 116 → 85, 6.1 %; 116 → 86, 6.4 %; total NO loss, 3.4 %.

Matrix effects

Loaded Pz solution (15 % w/w, 150 mg PZ/ml H_2O, loading 0.50 mol CO_2/mol amine) and various salts (1 mg salt/ml H_2O) commonly detected in PCC liquors were investigated for their effects on the analyte signal under the conditions specified in the section “Experimental conditions for standardisation of NPz in an aqueous matrix”.

Loaded Pz spiked with NPz: 50 μl of 0.5 loaded Pz solution (15 % w/w) was added to 400 μl dilute reference solution (dilution factor 1/100) and 1.55 ml charcoal filtered water. Final concentrations: 3.75 mg/ml loaded Pz; 4.84 ppm NPz. The results obtained are presented in Figure A5.2. The figure clearly shows strong ion suppression by Pz in the MS source.

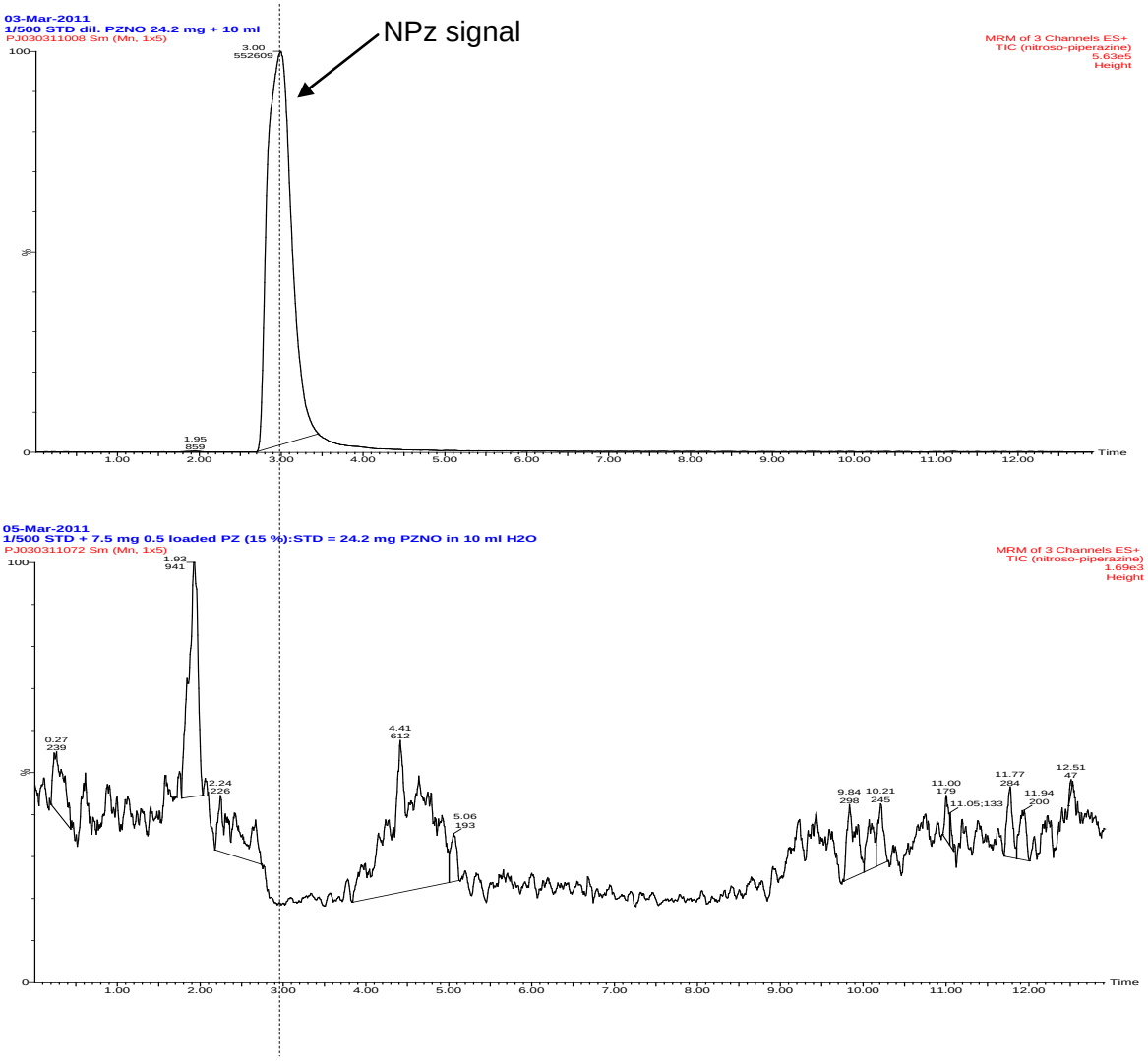


Figure 5.2. Complete signal suppression of 4.84 ppm NPz in the presence of 3.75 mg/ml loaded Pz solution (15 % w/w). Top: 4.84 ppm NPz in water; Bottom: in the presence of loaded Pz, [Pz] = 3750 ppm.

Approximately 0.2 mmol of formic acid (9.0 mg) was added to the sample and the sample was re-analysed. The result is presented in Figure 5.3.

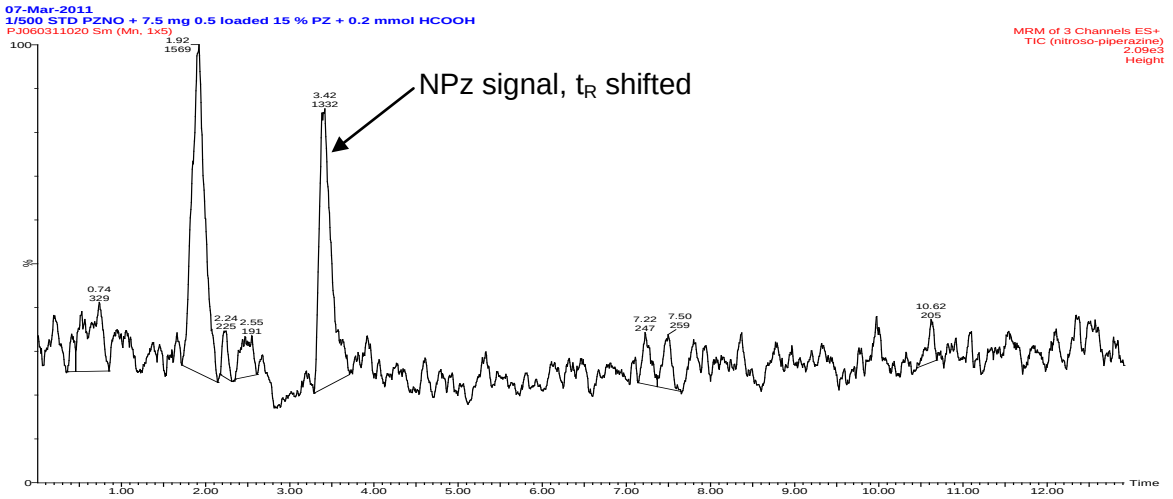


Figure 5.3. Effect of HCOOH addition (2 mmol) on the suppressed NPz signal (see Figure 5.2., bottom). A fraction of the original signal is recovered, however the peak t_R is shifted.

Signal recovery corresponds to 0.2 % of the original signal. The effect of the concentration of loaded Pz on NPz signal recovery was further analysed. Figure A5.4. demonstrates the effect of varying the Pz concentration on the signal recovered for NPz.

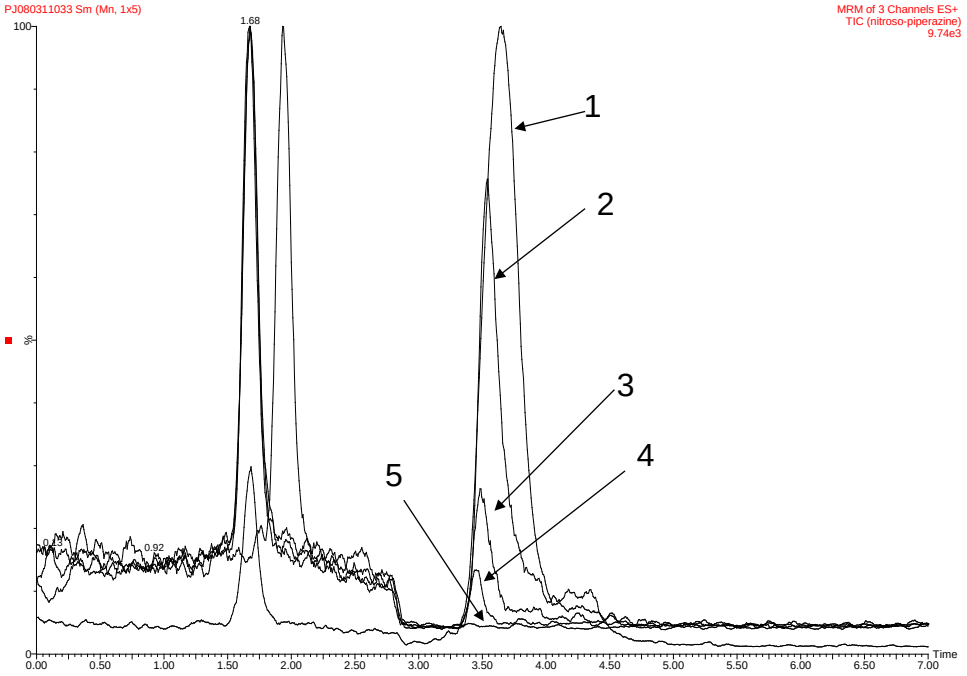


Figure 5.4. Effective signal suppression of NPz (4.84 ppm) analyte by loaded piperazine solution. 1 = 10 µl of 0.5 loaded 1.5 % Pz solution (75 ppm); 2 = 20 µl (150 ppm); 3 = 40 µl (300 ppm); 4 = 60 µl (450 ppm); 5 = 100 µl (750 ppm). No signal remains after addition of 100 µl. The peak at t_R = 1.5-2.5 mins is unidentified.

Figure 5.5. is a plot of the recovered signal versus concentration (ppm) of loaded Pz for each of the transitions being monitored. Best fit exponential curves for each transition are also presented, and can be used to estimate the degree of signal suppression for NPz.

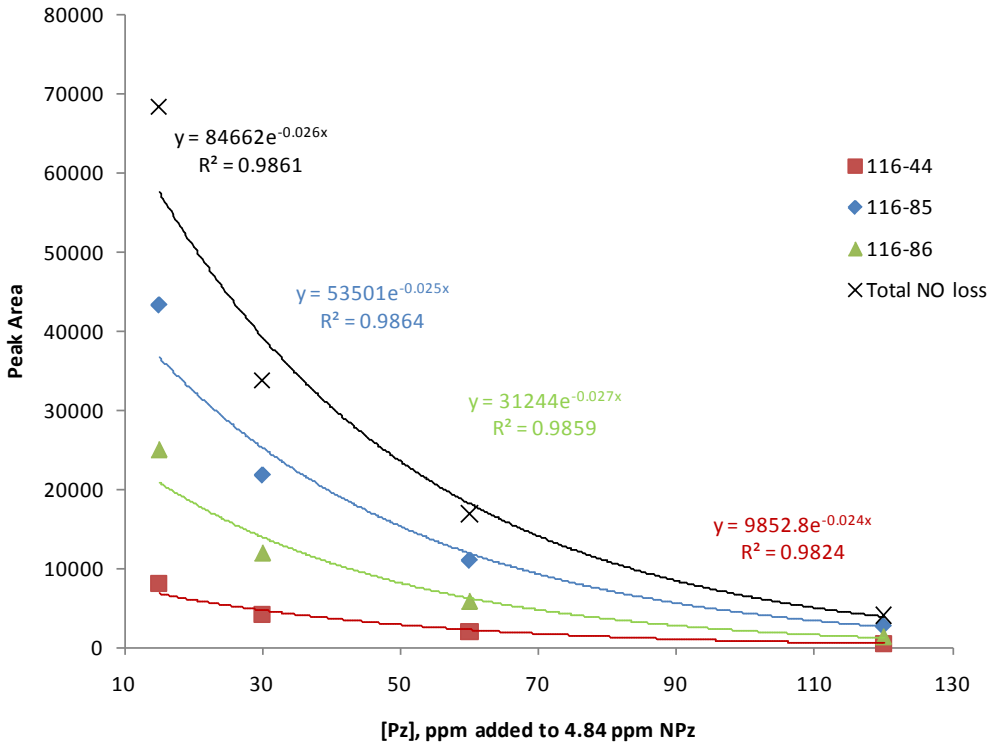


Figure 5.5. Recovered NPz signal versus [loaded Pz], (ppm) for each of the transitions being monitored.

At a concentration of 4.84 ppm NPz and 120 ppm, 99 % of the signal is suppressed. If the LOD in water (Table 5.1.) represents the signal measured when there is 99 % suppression by loaded piperazine, an estimate of the detection limit pertaining to NPz in loaded solutions can be determined for each transition (assuming the suppression effect is linear with [NPz]). For M/z 116 → 44, LOD = 5.1 ppm; M/z 116 → 85, LOD = 0.26 ppm; M/z 116 → 86, LOD = 0.60 ppm.

The values in Table 5.1. can also be used to estimate the maximum tolerable concentration of loaded Pz which can be present with NPz before complete signal suppression. For M/z 116 → 44, [Pz] = 112 ppm; M/z 116 → 85, [Pz] = 213 ppm; M/z 116 → 86, [Pz] = 174 ppm. These values assume [Pz] is not limiting. Due to the strong ion-pairing nature of the analyte, it is recommended that this method is only applied to wash- and discharge waters when [Pz] < 150 ppm, preferably when [Pz] < 100 ppm.

Other salts: Salts commonly encountered in PCC liquors (section B.8, Materials) were also investigated for their signal suppressing effect: [salt] = 1000 ppm, [Npz] = 4.84 ppm. The extent of signal suppression (across all transitions) at 1000 ppm was: KNO_3 (nitrate) 97-99 %; Na_2SO_4 (sulfate) 98 %; $H_2C_2O_4$ (oxalate) 86-92 %; $NaHCO_3$ (bicarbonate) 89-91 %; CH_3COONH_4 (acetate) 78-81 %. Although it is unlikely these salts will be encountered at such high concentrations in PCC liquors, the results highlight the deleterious effect of buffers on MS detection, even for “MS-friendly” buffers such as ammonium acetate and bicarbonate. It is likely that formation of 4-nitrosopiperazine-1-carboxylate ($ON\text{-}NC_4H_4N\text{-}CO_2^-$) also contributes to the decrease in NPz signal when bicarbonate is added to NPz solutions.

A common chromatographic feature in the presence of salts was significant peak tailing, as demonstrated in Figure 5.6. for ammonium acetate.

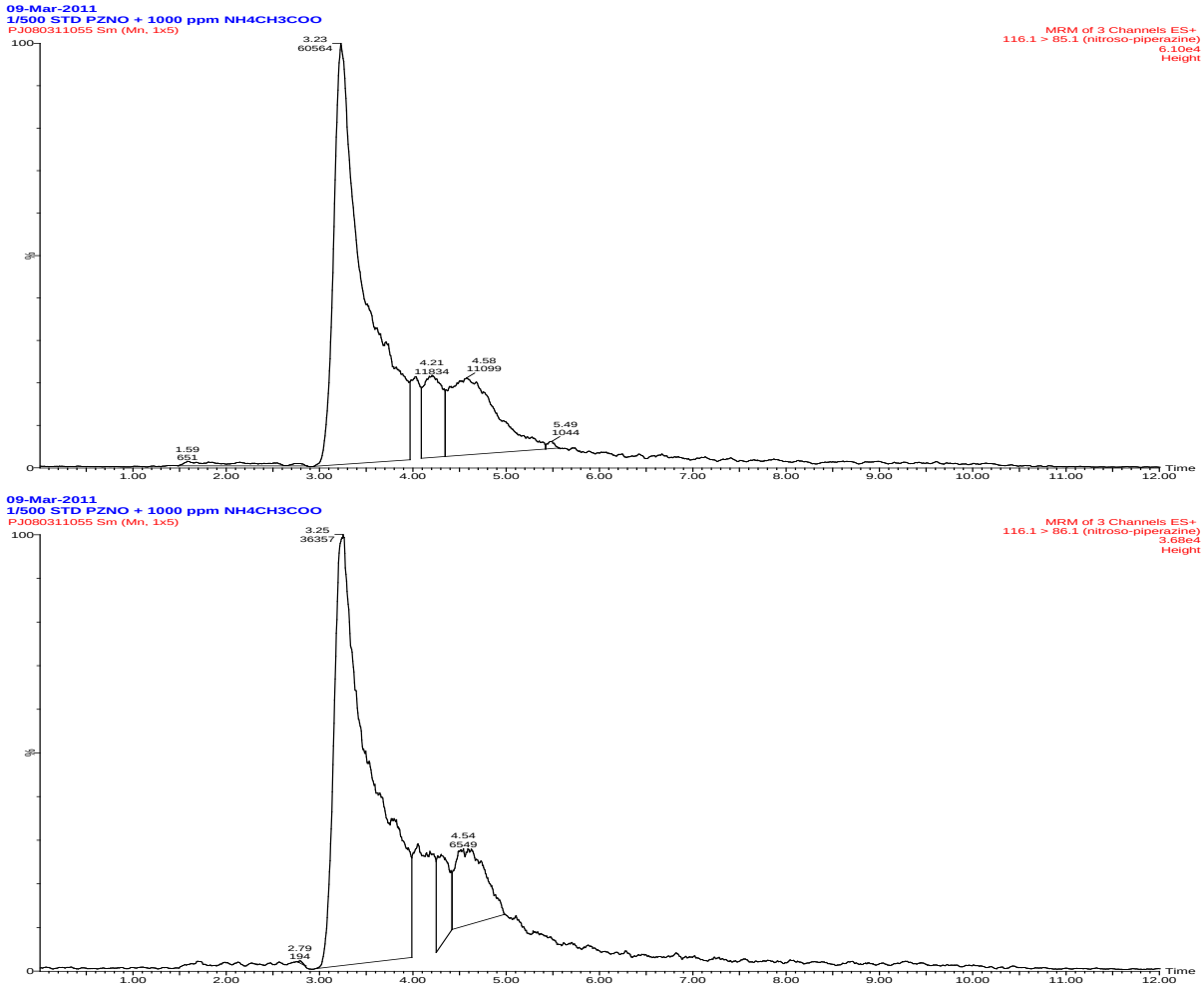


Figure 5.6. M/z 116 → 85 (top) and M/z 116 → 86 (bottom) transitions for 4.84 ppm NPz in the presence of 1000 ppm CH_3COONH_4. The addition of buffers to the mobile phase for improved chromatographic peak shapes is not recommended when MS detection is used, due to ion-pairing in the MS source.

Blind spiking trial/recovery test

Test samples: 8 test samples were prepared as follows: 160 µl of dilute (factor = 1/100) 15 % loaded Pz solution, [loaded Pz] = 120 ppm, was added to each of the 8 vials. 200 µl of dilute reference solution was added to one vial ([NPz] = 2.4 ppm), and 20 µl added to another ([NPz] = 0.24 ppm). The volumes of all test samples were made to 2 ml using charcoal-filtered water.

Direct analysis: 40 µl of each sample was analysed using HPLC-MS/MS. The results for Unknown sample 4 are presented in Figure 5.7. Identification of the sample containing 0.24 ppm using direct analysis was not possible.

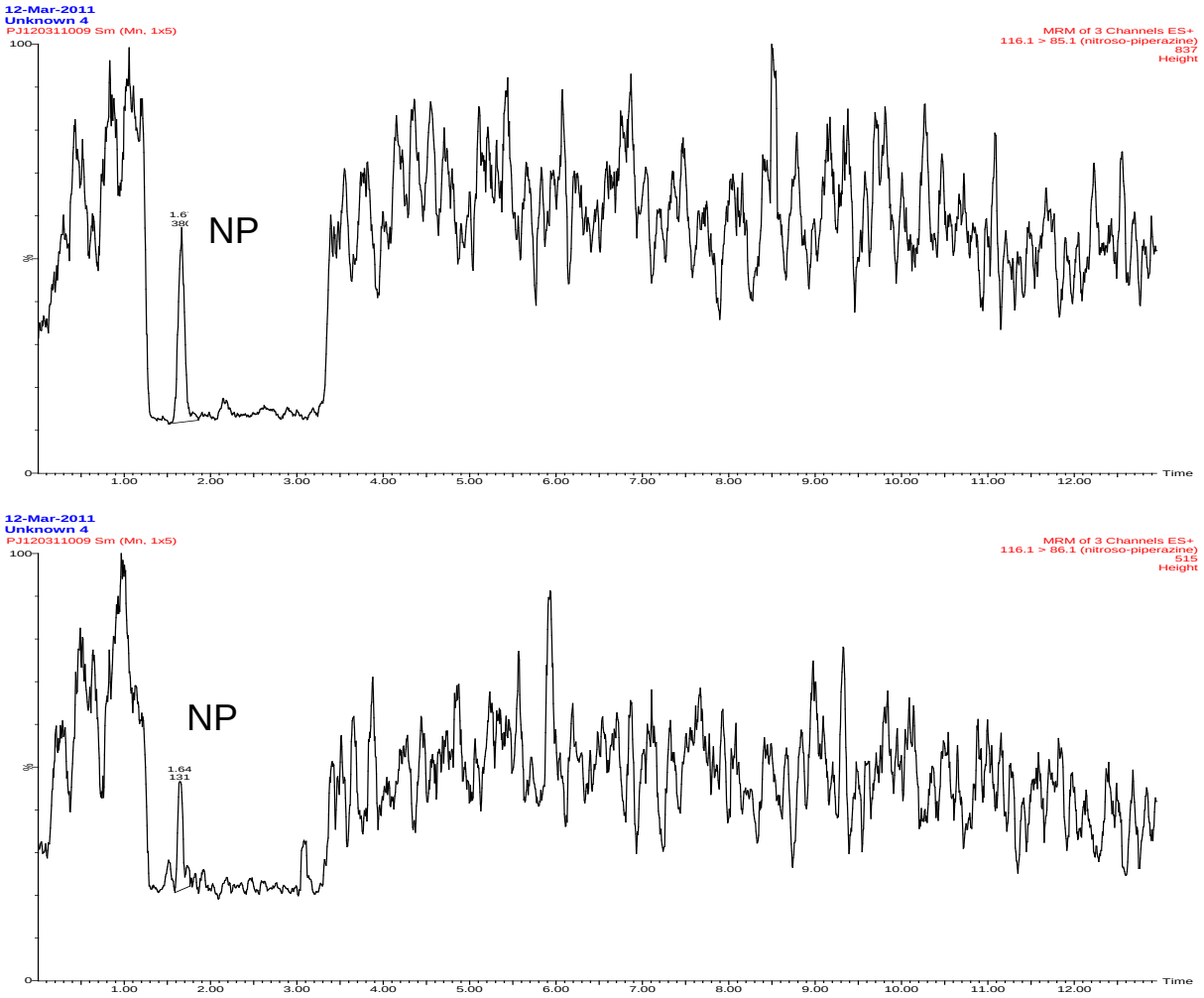


Figure 5.7. M/z 116 → 85 (top) and M/z 116 → 86 (bottom) transitions for Unknown sample 4. The NPz peaks are highlighted in each chromatogram.

It has been confirmed that Unknown sample 4 contained 2.4 ppm NPz.

Sub-sample spike with 1 ppm NPz: A test portion (1 ml) of each unknown sample was was added to 100 µl of dilute (factor = 1/100) reference solution, 10 µl HCOOH and 890 µl charcoal-filtered water (total test sample volume 2 ml, [NPz (spike)] = 1.2 ppm. Each sample was then analysed using HPLC-MS/MS. These are currently being run

Comments/Summary
Several attempts were made to separate NPz from the loaded piperazine matrix using the following techniques:

(i) acid-functionalized SPE cartridges and buffer solutions in the pKa range 7.5-11

(ii) RDX-Porapak cartridges (used for nitro explosive detection at ppb levels)

(iii) IC-MRM using an acidic mobile phase (formic acid, see Method for NDELA detection in PCC liquors)

Separations were not clean enough using any of these methods to warrant a pre-analysis sample work-up. Other SPE phases - considered artefact-prone for gas phase sample

collection, such as activated charcoal and Florasil - were not considered, as there is no justification for the belief that pre-concentration would be artefact-free in the condensed phase (in the presence of nitrite ions/nitrous acid and oxygen). Thermosorb N produces too many MS artefacts for use in LC-MS/MS.
The high propensity for NPz to form ion-pairs in the atmospheric MS source results in lower detection limits in the presence of loaded Pz and salts. *The profound effect of piperazine within the sample matrix suggests [NPz] that is quantifiable is several orders of magnitude lower than the true concentration in the test sample.* The method described is limited to solutions with low Pz and salt concentrations, such as wash- or discharge waters.

References

Jackson, P.; Attalla, M.I. (2010) N-Nitrosopiperazines form at high pH in post-combustion capture solutions containing piperazine: a low-energy collisional behaviour study. *Rapid Commun. Mass Spectrom.* 24: 3567–3577.

Appendix (Section 5)

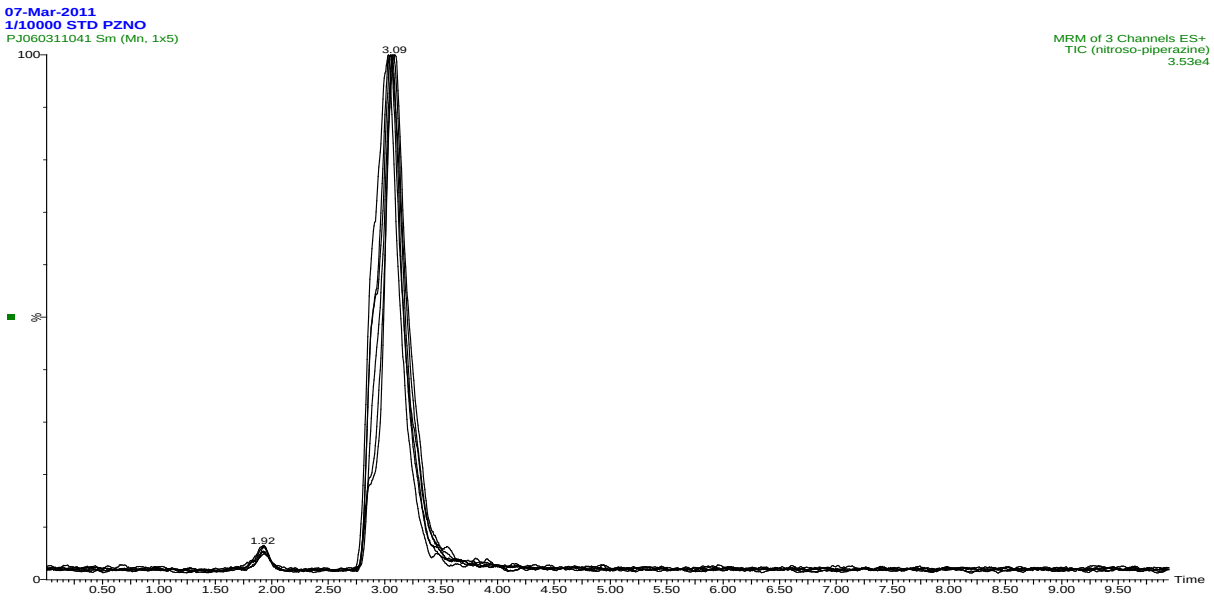


Figure 5.8. Results for 6 repeat injections of 40 μl (separated by blank samples) over two days for NPz reference solution, [NPz] = 242 ppb. Total ion chromatograms (sum of three transitions monitored) shown.

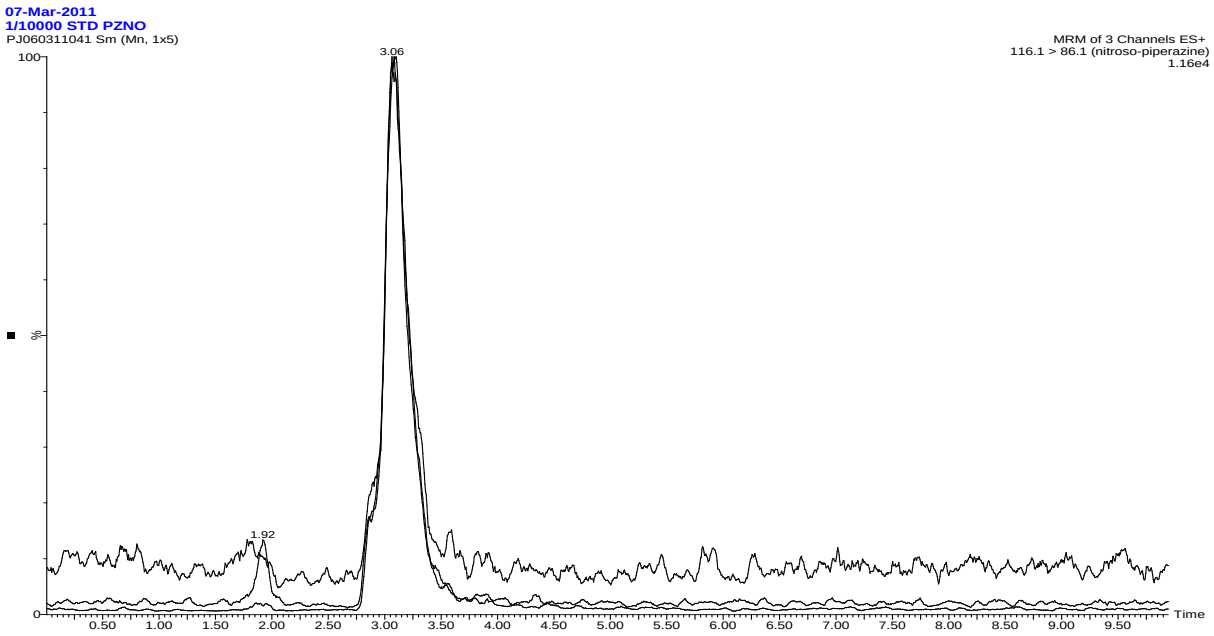


Figure 5.9. Overlay of ion chromatograms m/z 116 → 44, m/z 116 → 85, m/z 116 → 86 for npz reference solution, [npz] = 242 ppb

6. DETERMINATION BY LC-MS-MS OF N-NITROSAMINES IN SOLVENTS AND WATERS (IMPINGER SOLUTIONS)

Title: Determination by LC-MS-MS of N-nitrosamines in solvents and waters

Authors: Advanced Analytical Australia Pty Ltd (specifically, Rama Nimmagadda)

Scope: This method is for the determination of total volatile N-nitrosamines in PCC solvents.and waters

Summary:

- N-nitrosamines were determined at lower concentrations by using solid phase extraction and LC-MS-MS.
- Sample A10-4110-2 (30% w/w MEA/ 1M KHCO3) was used as blank matrix to perform the analysis of N-nitrosoamines.
- EPA 8270 Appendis IX Nitrosoamine mix was used to prepare standard solutions. The spiked solutions were left at room temperature for 2 hours before the extraction.
- Three 5 mL aliquots were transferred into plastic bottles and two of these bottles were spiked at 100 ppb (50 µl of 10 ppm) and 500 ppb (250 µl of 10 ppm) and mixed well.
- All these three bottles were diluted to 100 mL with de-ionized water and shaken well. Hydrophilic-Lipophilic Balance Sorbent (HLB) solid phase cartridges were used to extract these solutions.
- Similarly, 5 mL of impinger solution and a spike at 200 ppb (100 µl of 10 ppm solution) were analysed.
- In both cases N-Nitrosodimethylamine was not detected. The MRM transitions for the remaining analytes are represented in the following figures (Figures. 6.1 – 6.19).

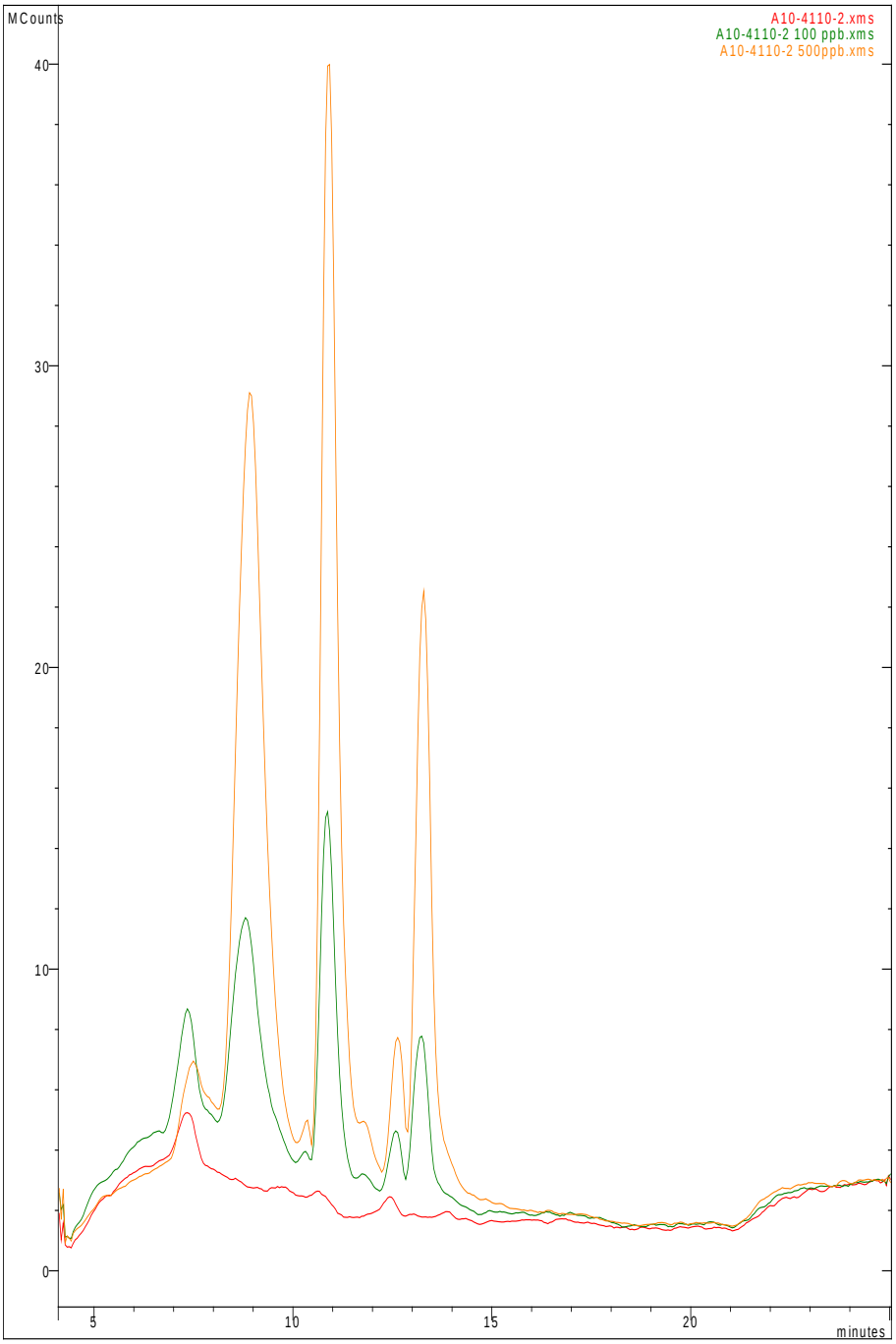


Figure 6.1. Total ion chromatogram for A10-4110-2, Spike 100 ppb and Spike 500 ppb

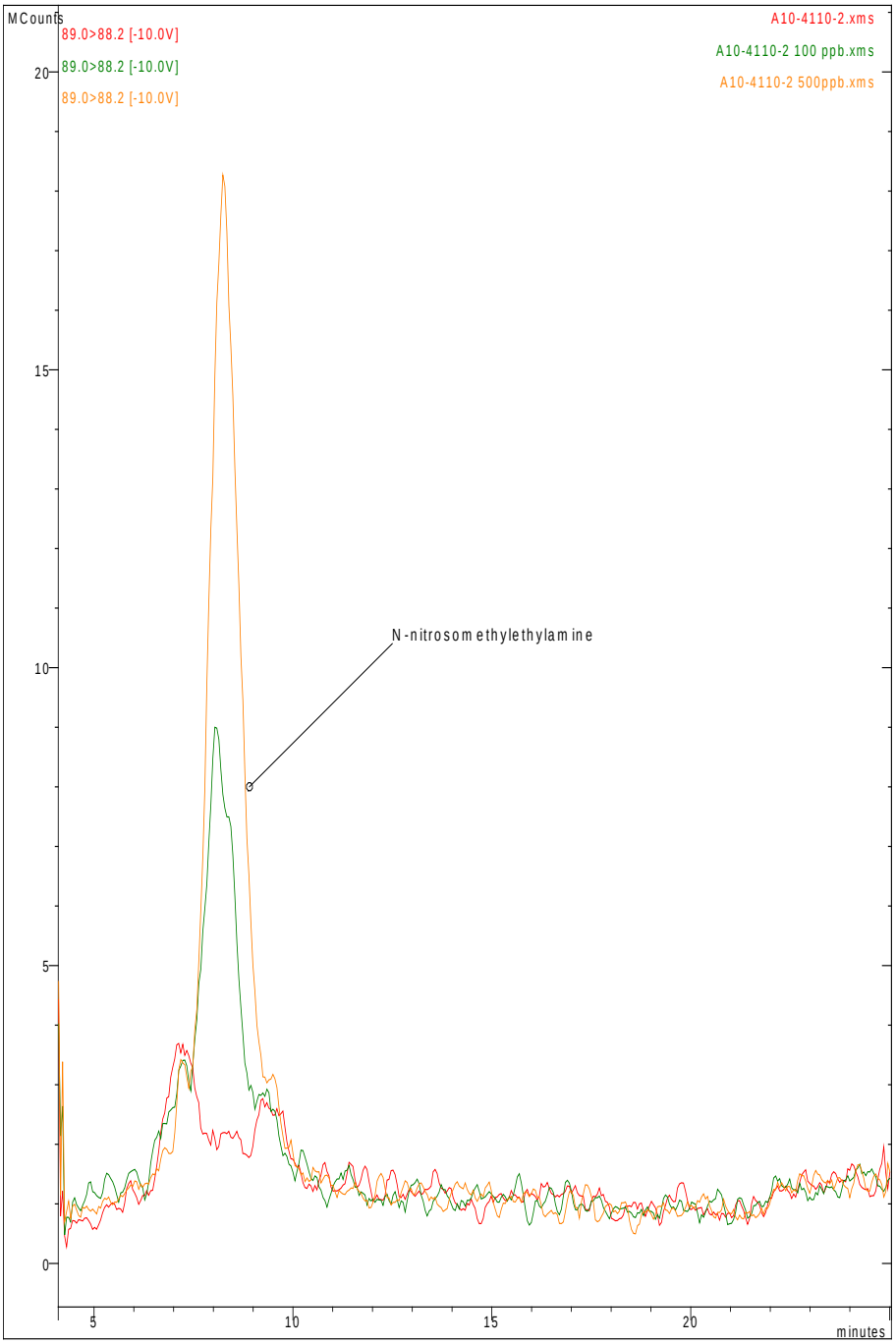


Figure 6.2. MRM for N-Nitrosomethylethylamine in A10-4110-2, Spike 100 ppb and Spike 500 ppb

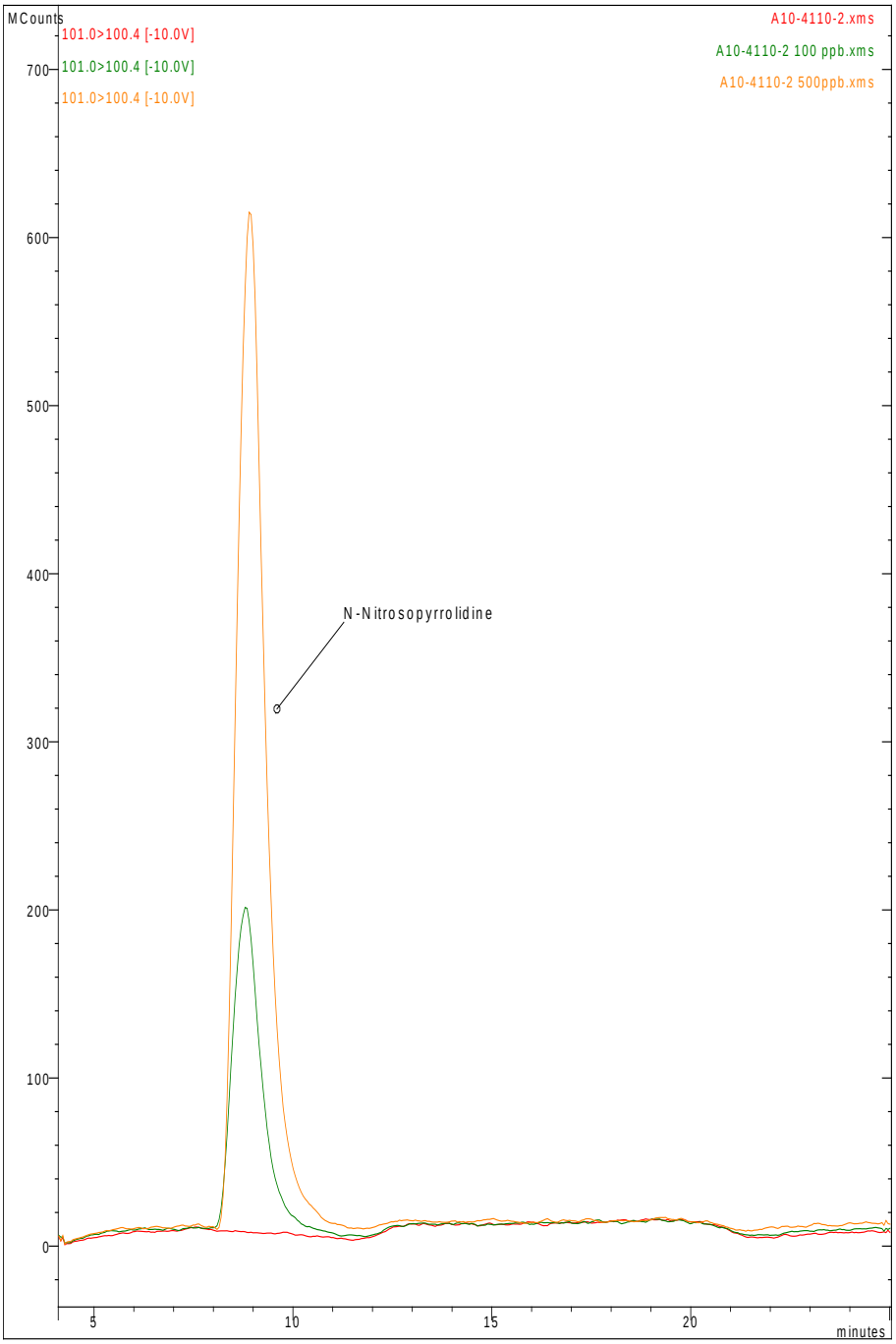


Figure 6.3. MRM for N-Nitrosopyrrolidine in A10-4110-2, Spike 100 ppb and Spike 500 ppb

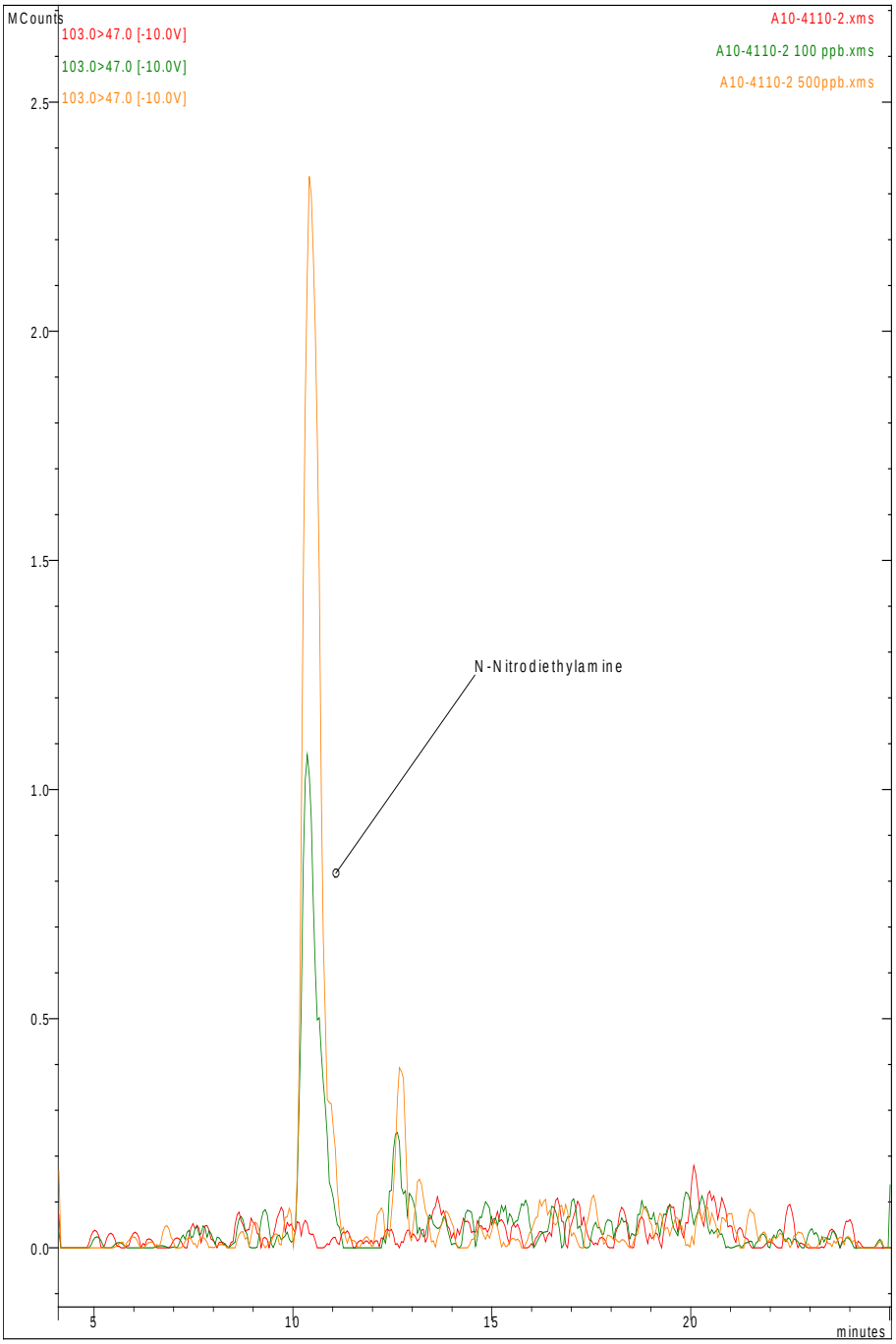


Figure 6.4. MRM for N-Nitrosodi-ethylamine in A10-4110-2, Spike 100 ppb and Spike 500 ppb

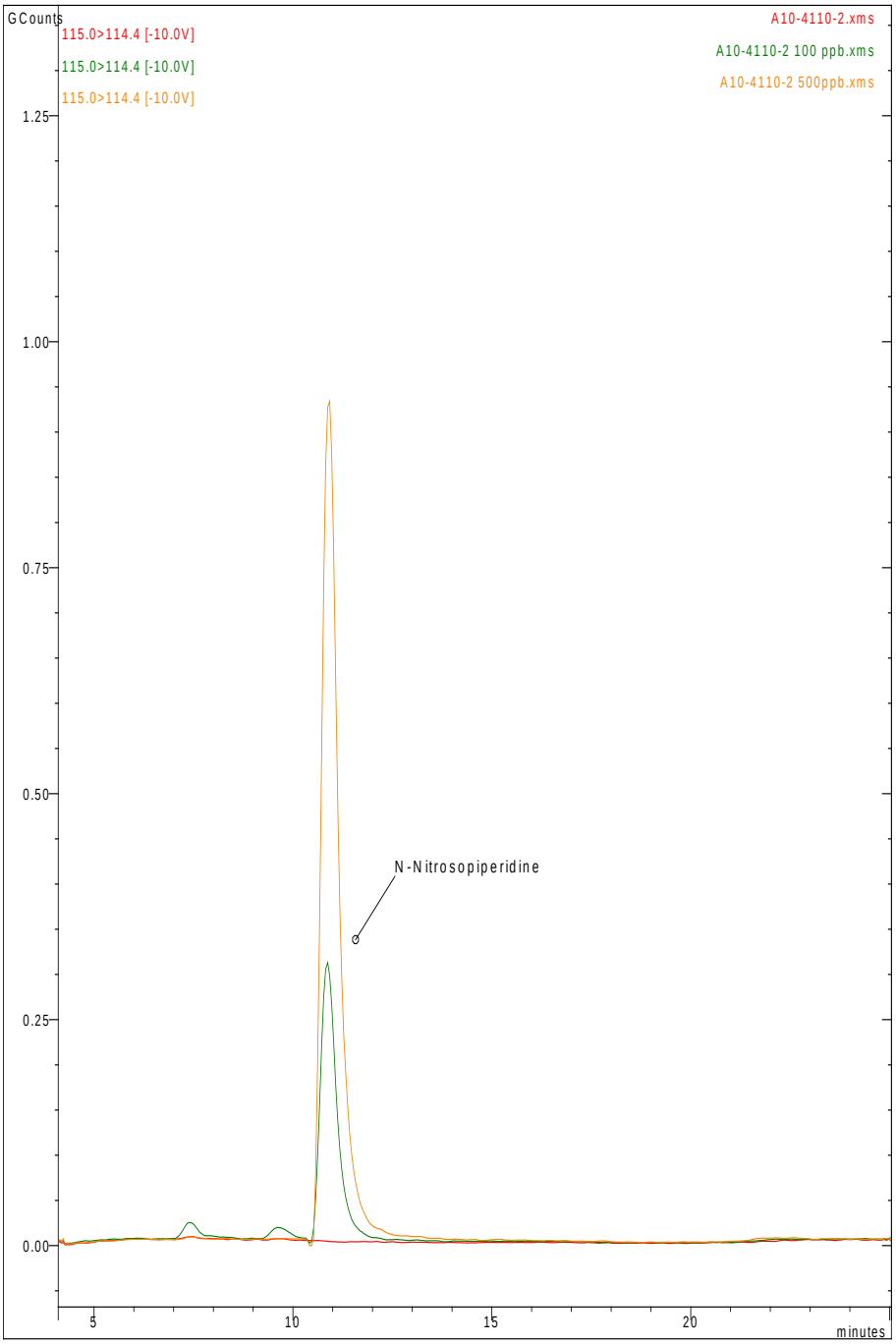


Figure 6.5. MRM for N-Nitrosopiperidine in A10-4110-2, Spike 100 ppb and Spike 500 ppb

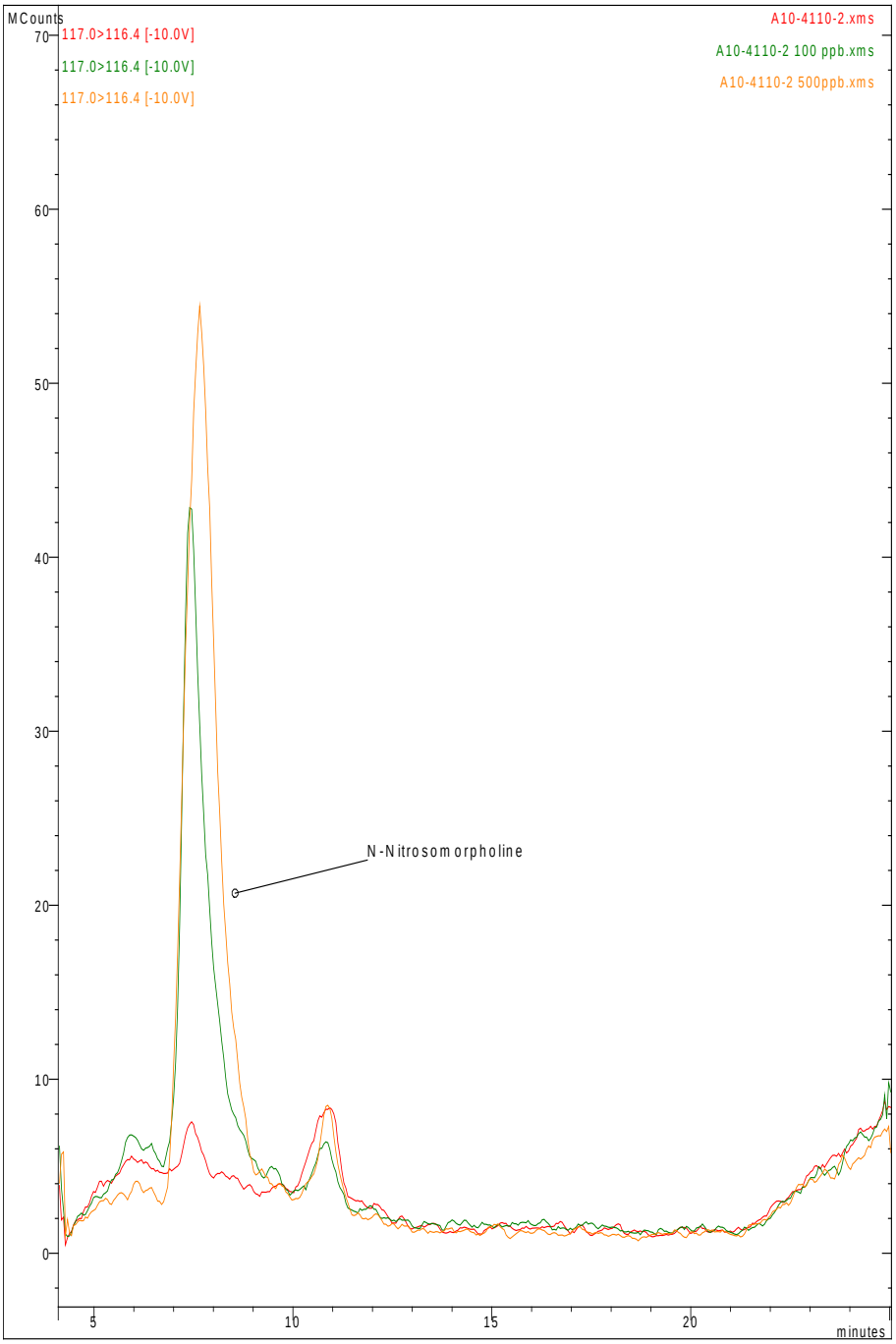


Figure 6.7. MRM for N-Nitrosomorpholine in A10-4110-2, Spike 100 ppb and Spike 500 ppb

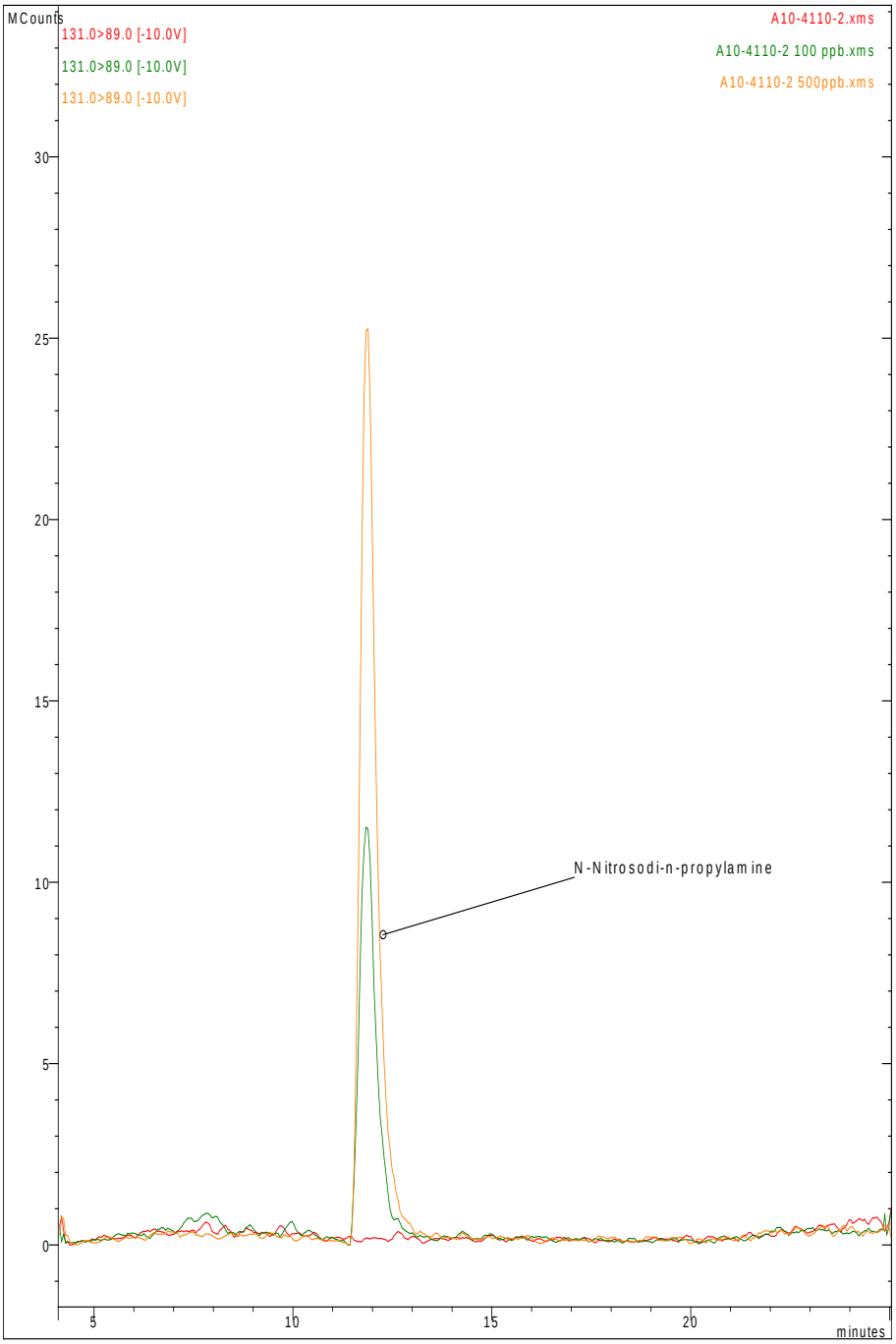


Figure 6.8. MRM for N-Nitrosodi-n-propylamine in A10-4110-2, Spike 100 ppb and Spike 500 ppb

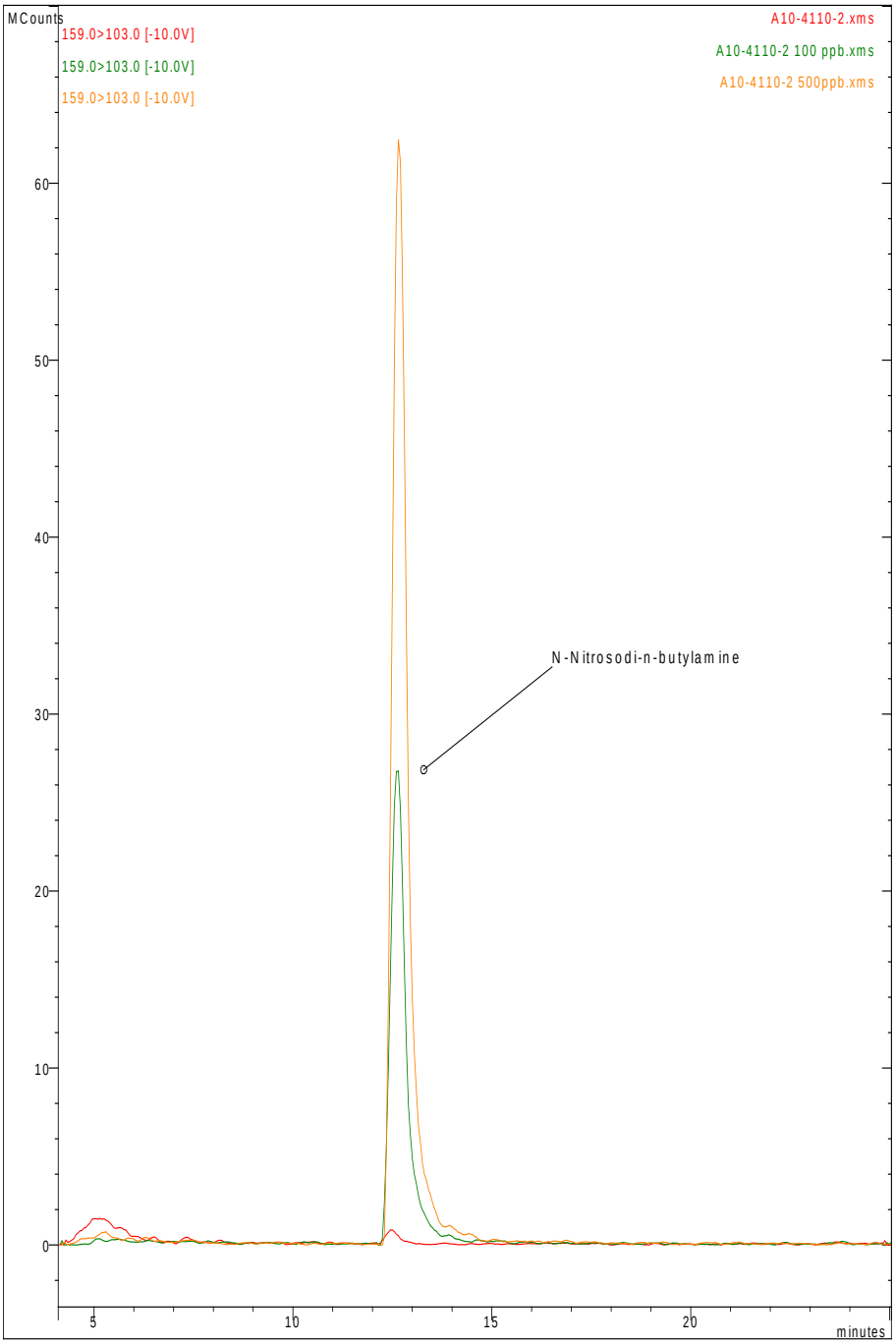


Figure 6.9. MRM for N-Nitrosodi-n-butylamine in A10-4110-2, Spike 100 ppb and Spike 500 ppb

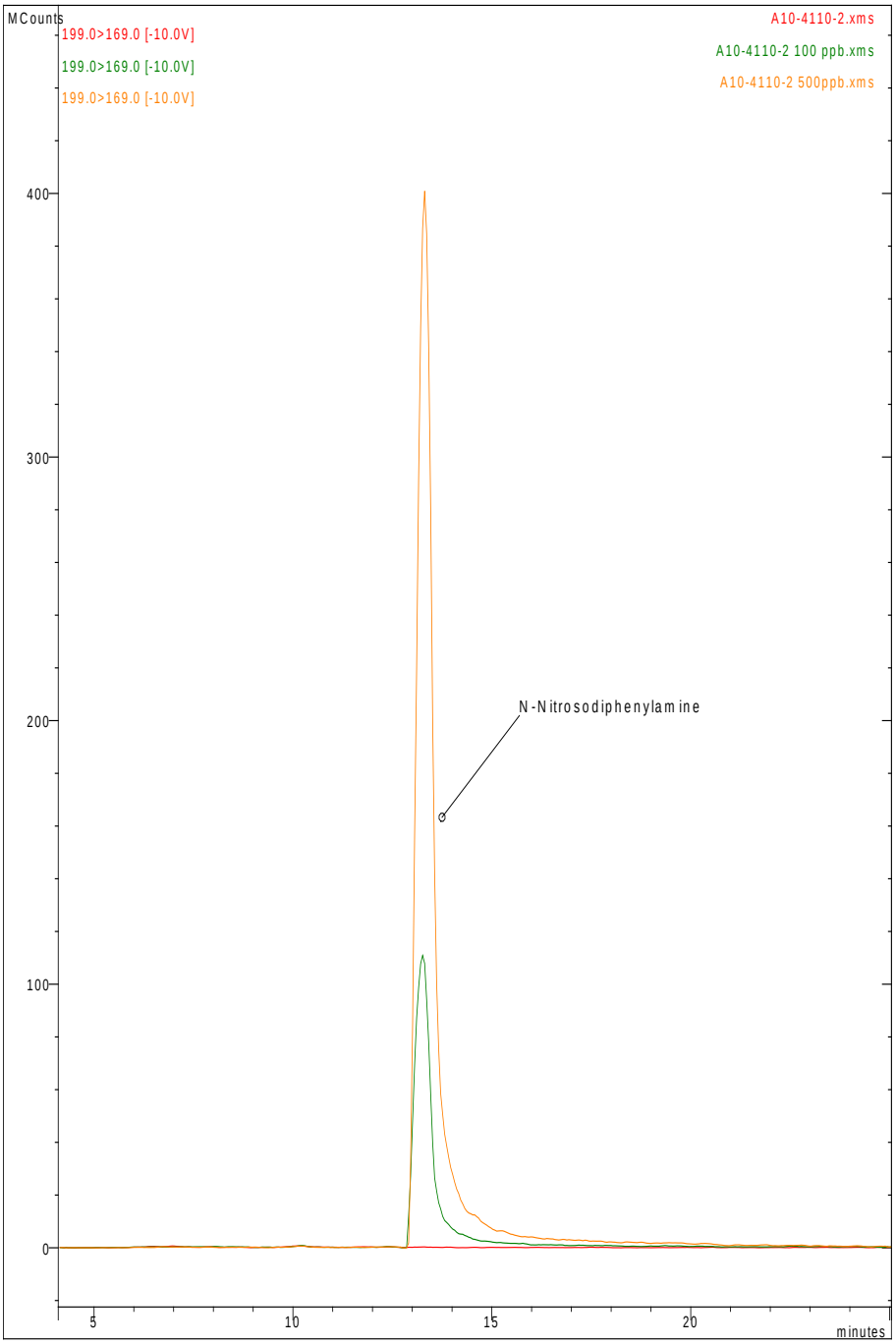


Figure 6.10. MRM for N-Nitrosodi-n-phenylamine in A10-4110-2, Spike 100 ppb and Spike 500 ppb

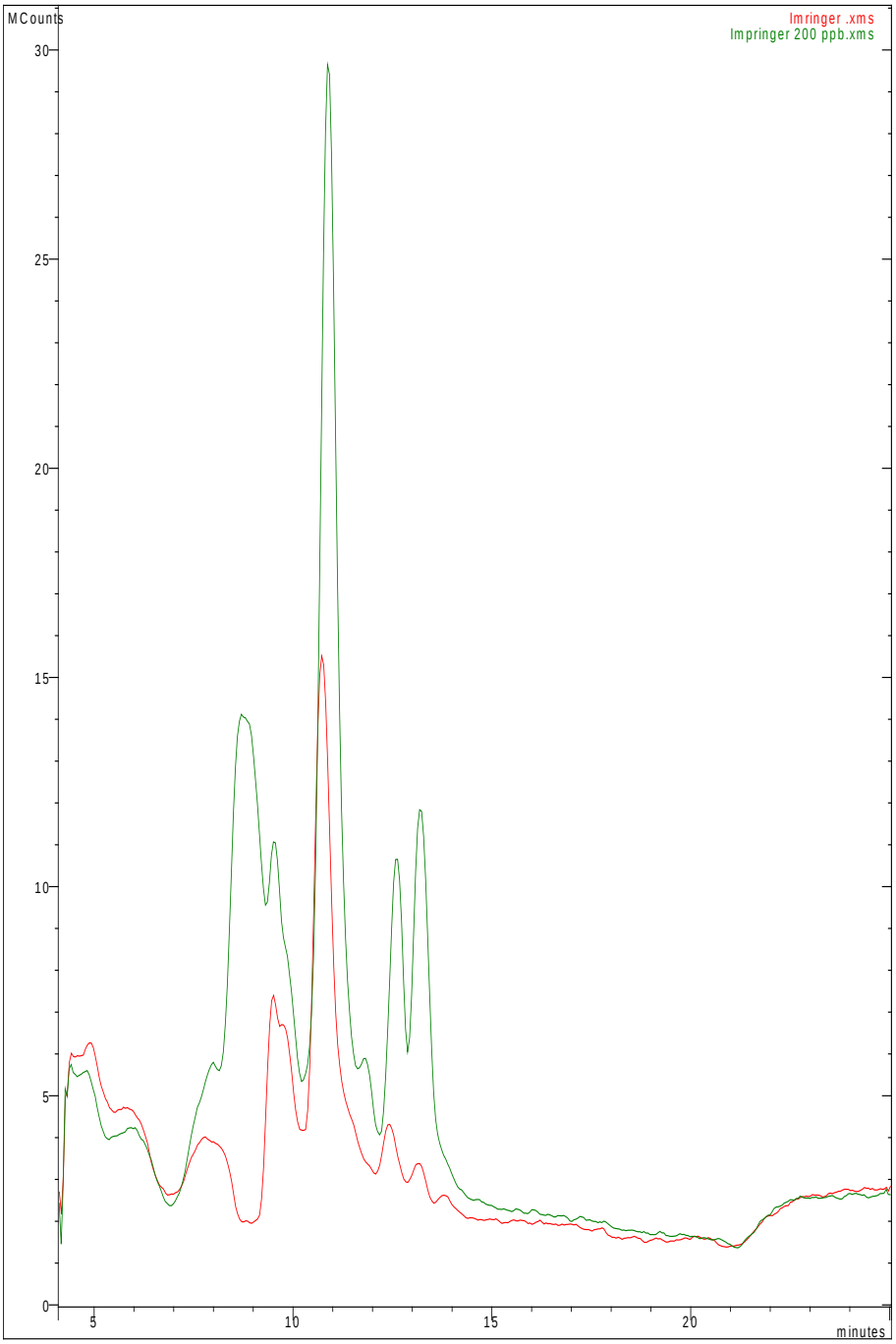


Figure 6.11. Total ion chromatogram for impinger solution and the spike at 200 ppb

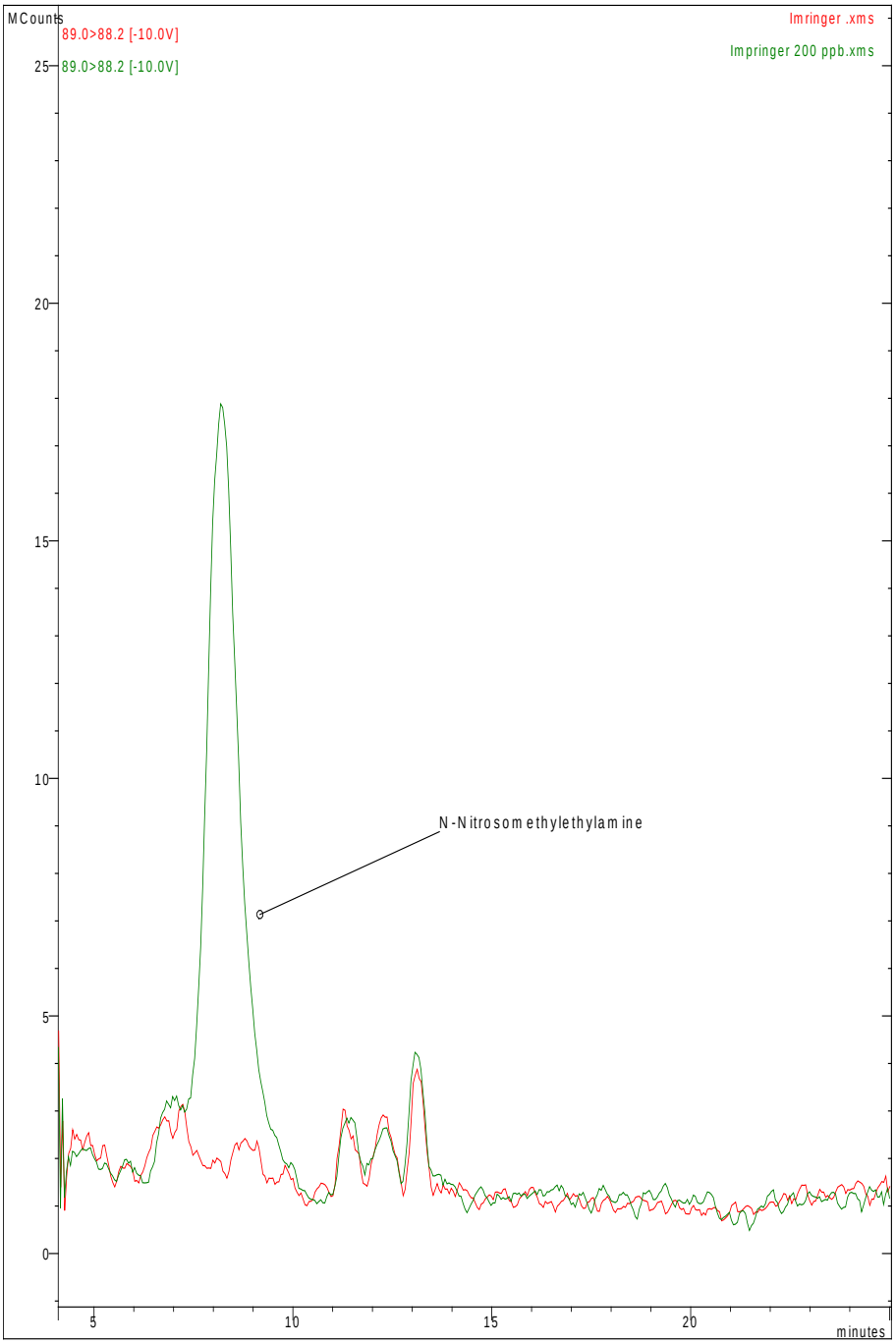


Figure 6.12. MRM for N-nitrosomethylethylamine in impinger solution and the spike at 200 ppb

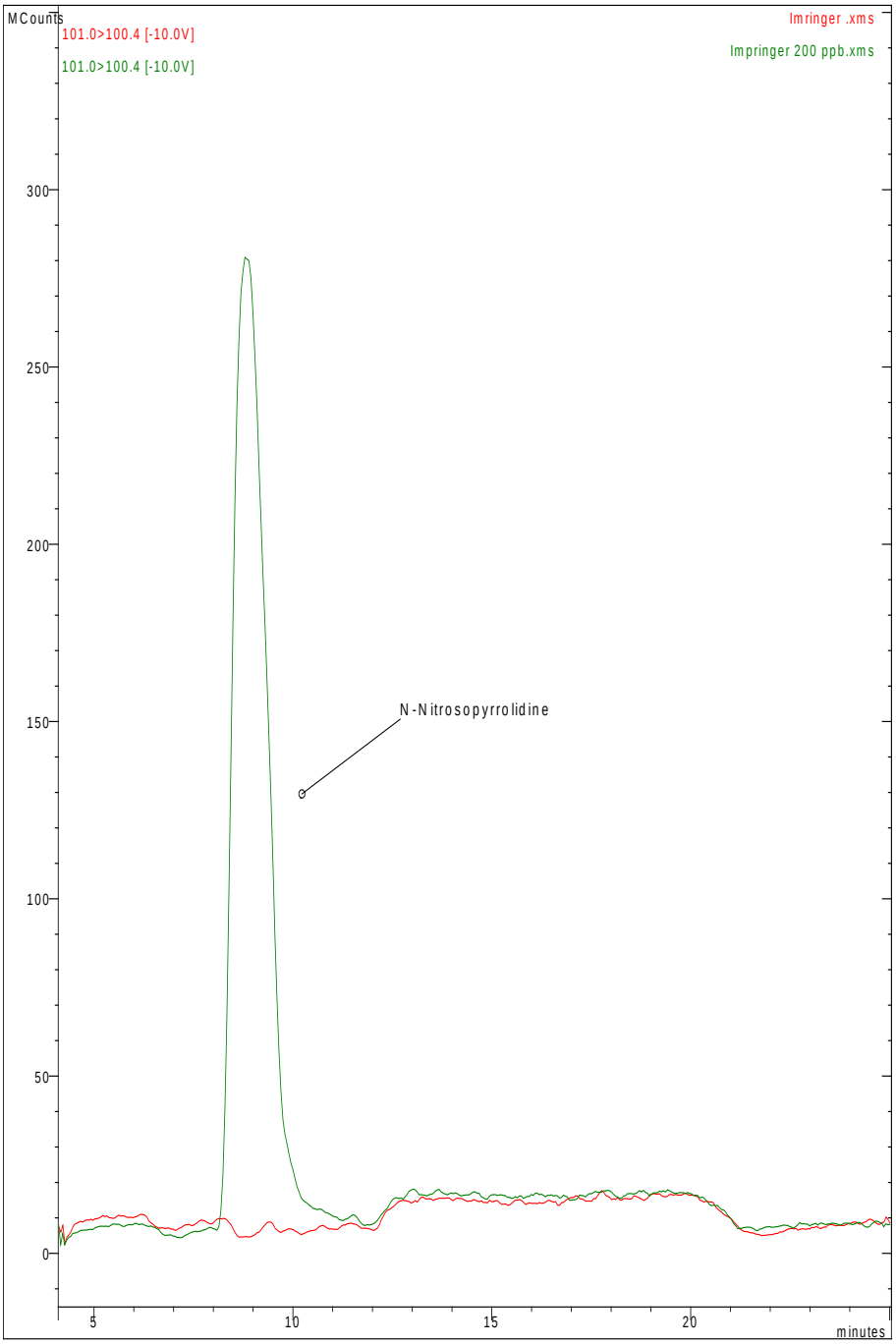


Figure 6.13. MRM for N-nitrosopyrrolidine in impinger solution and the spike at 200 ppb

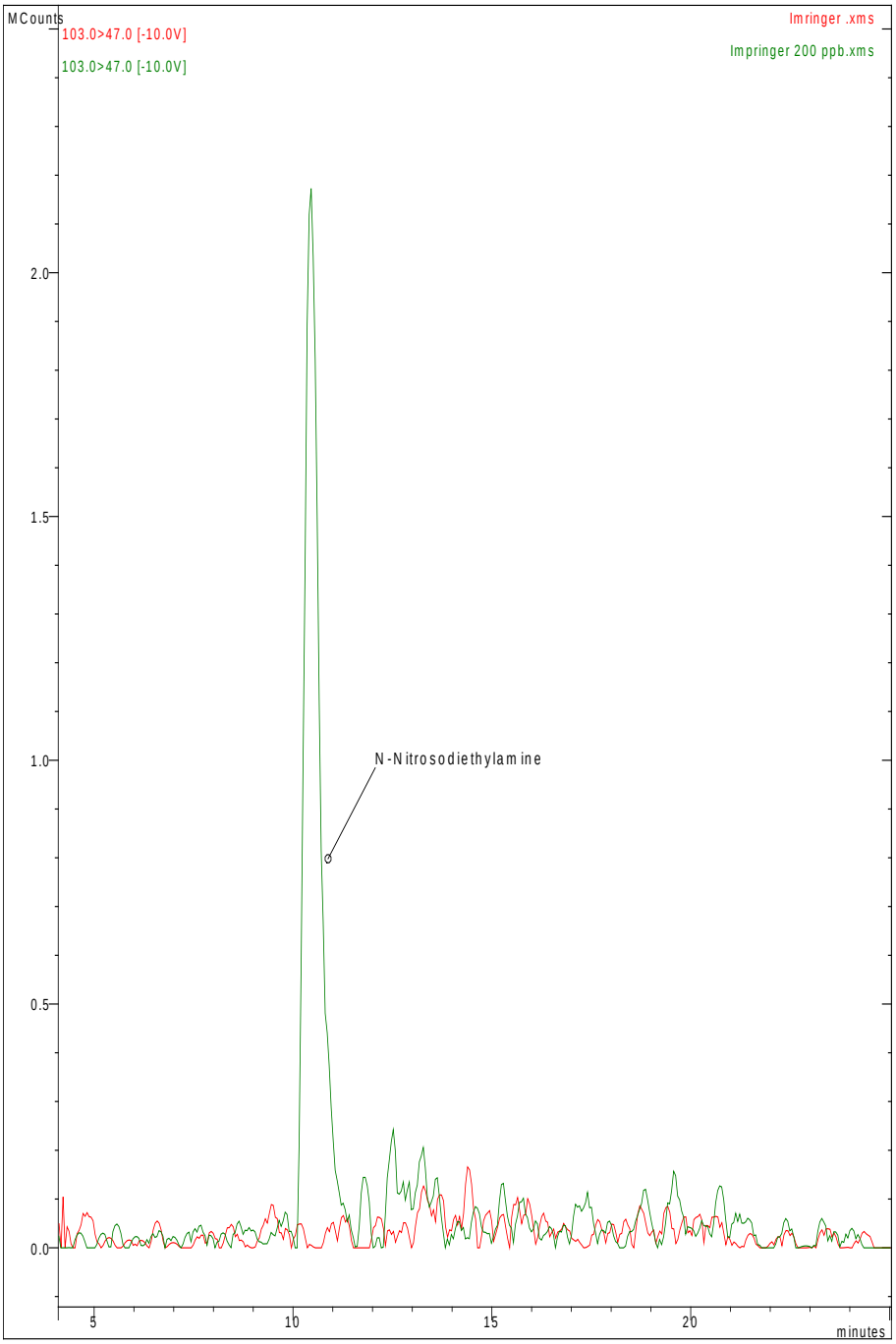


Figure 6.14. MRM for N-nitrosodiethylamine in impinger solution and the spike at 200 ppb

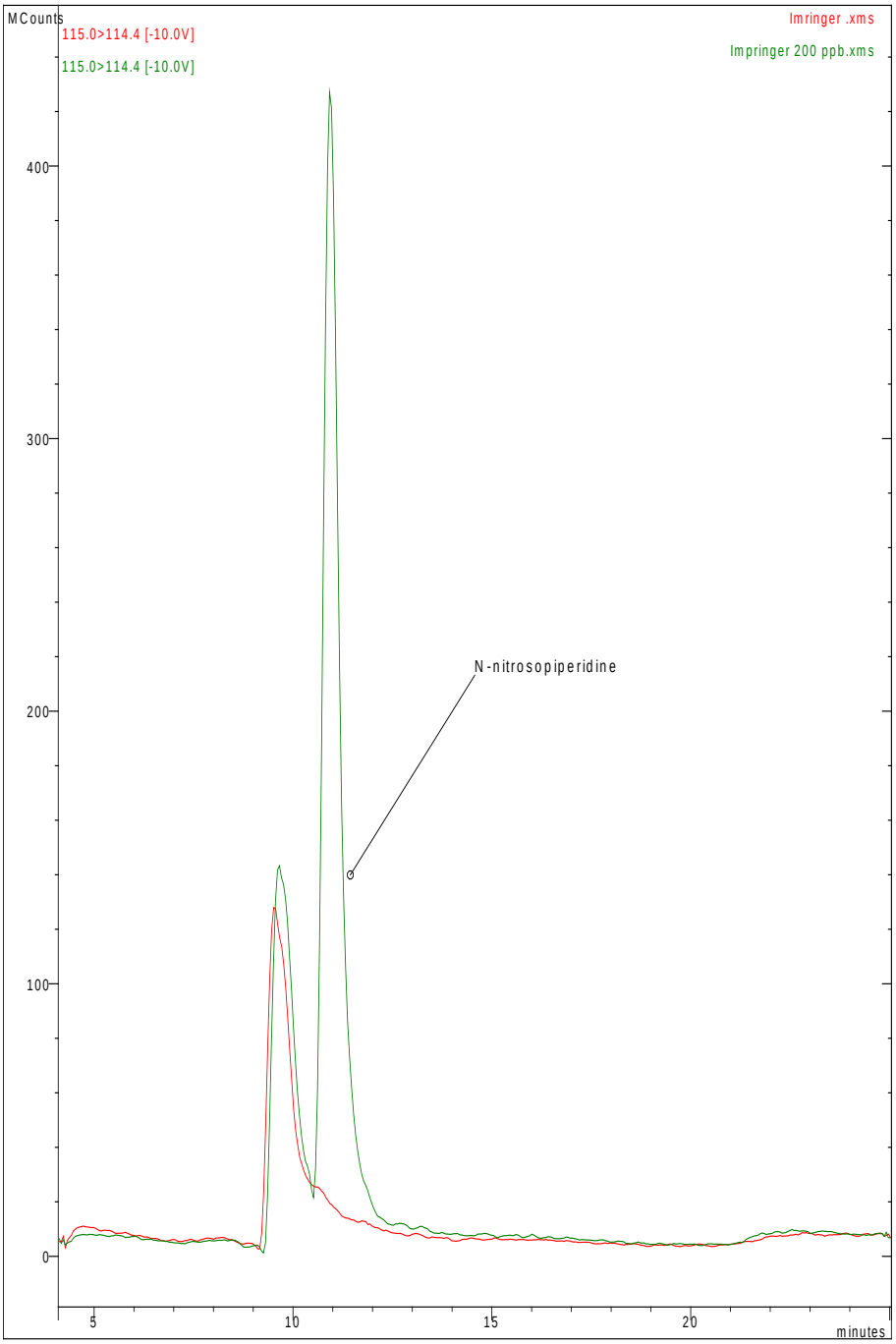


Figure 6.15. MRM for N-nitrosopiperidine in impinger solution and the spike at 200 ppb

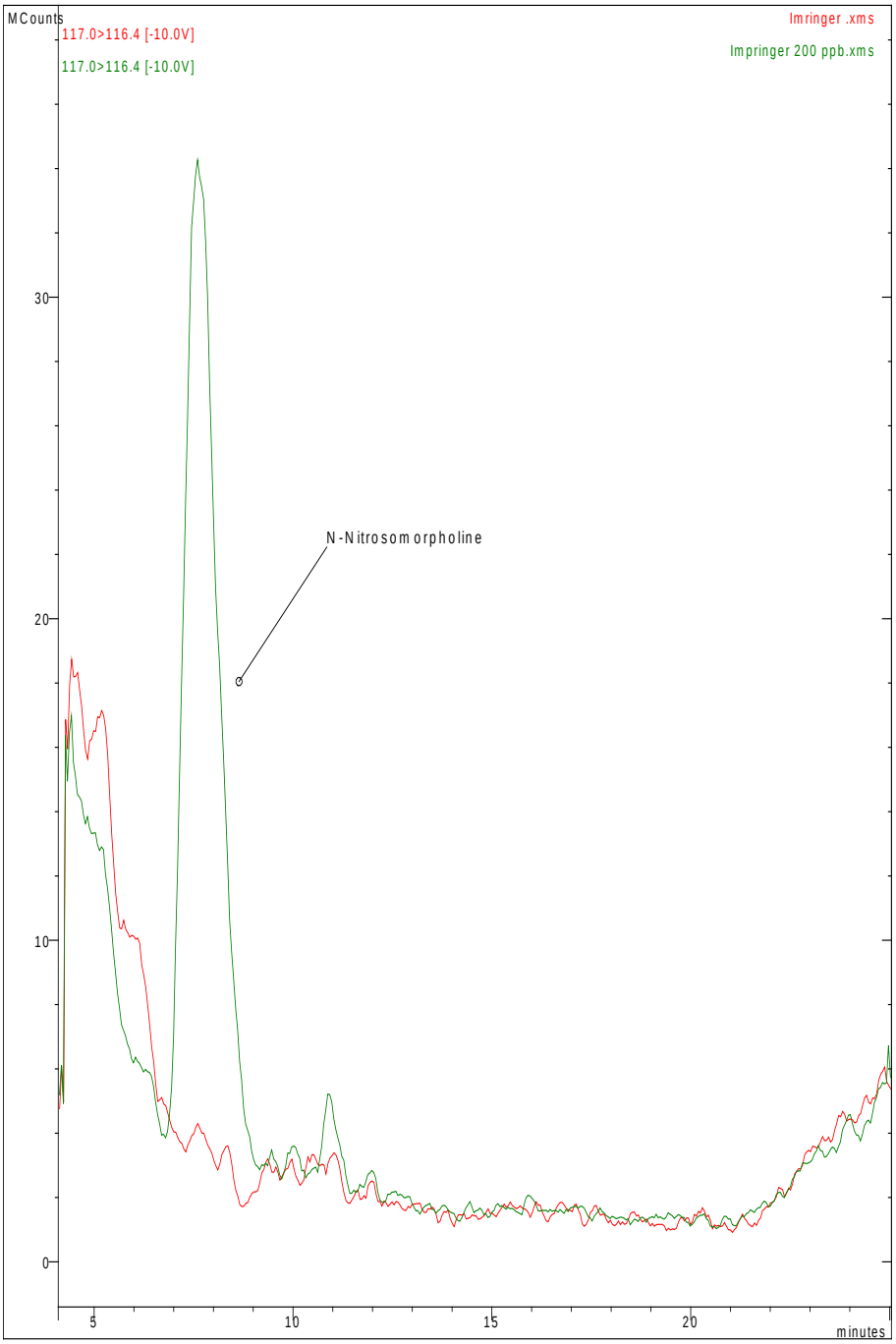


Figure 6.16. MRM for N-nitrosomorpholine in impinger solution and the spike at 200 ppb

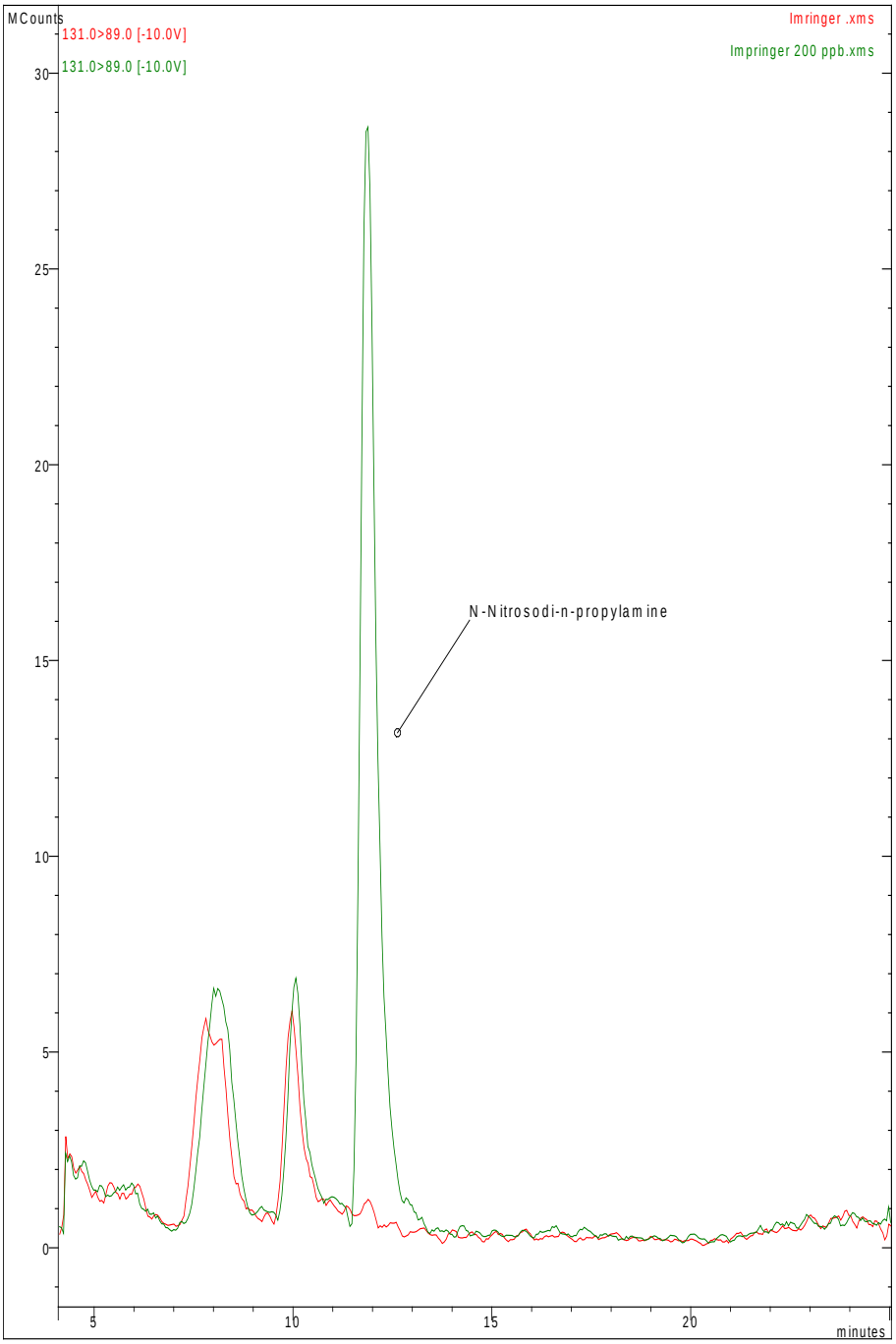


Figure 6.17. MRM for N-nitrosodi-n-propylamine in impinger solution and the spike at 200 ppb

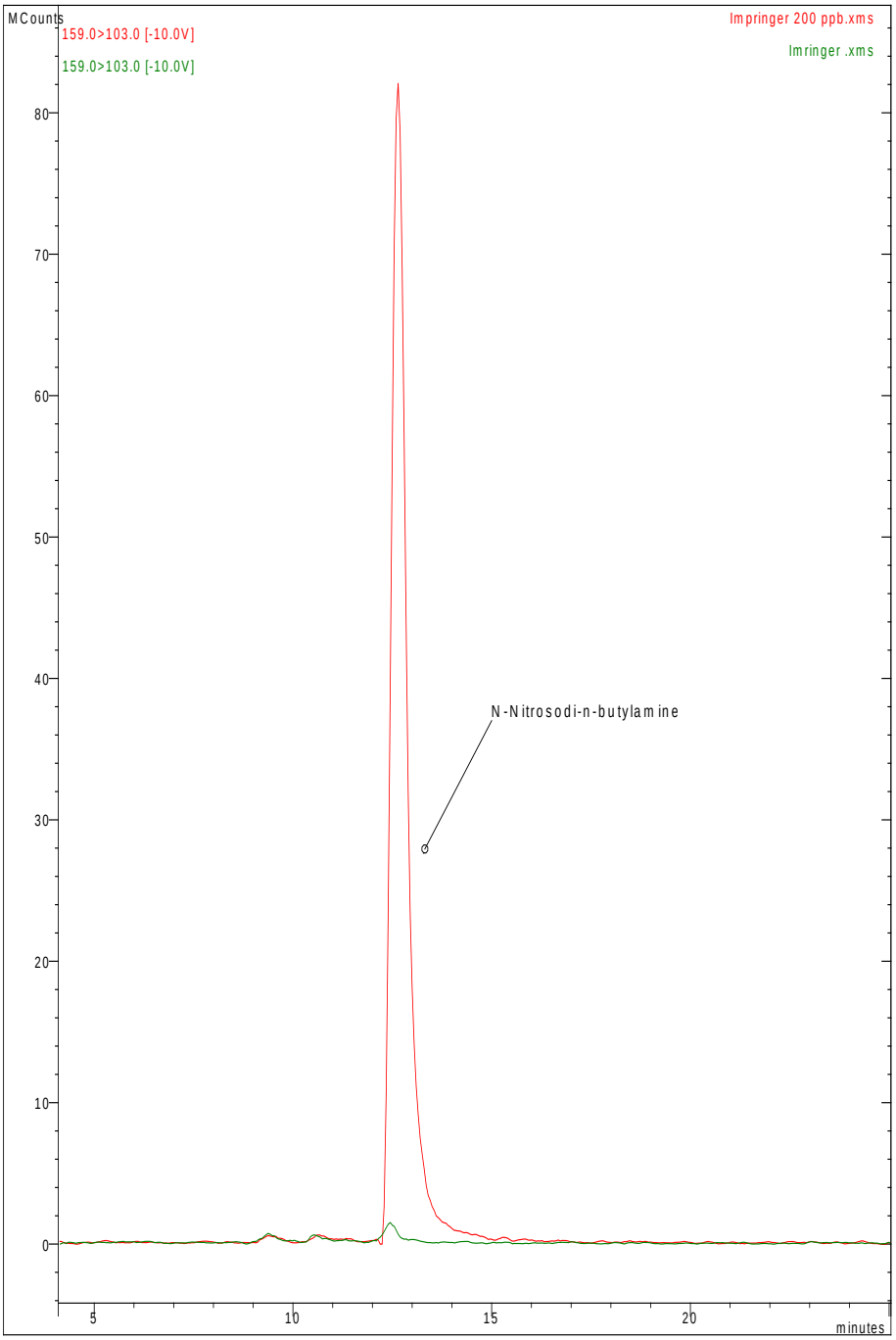


Figure 6.18. MRM for N-nitrosodi-n-butylamine in impinger solution and the spike at 200 ppb

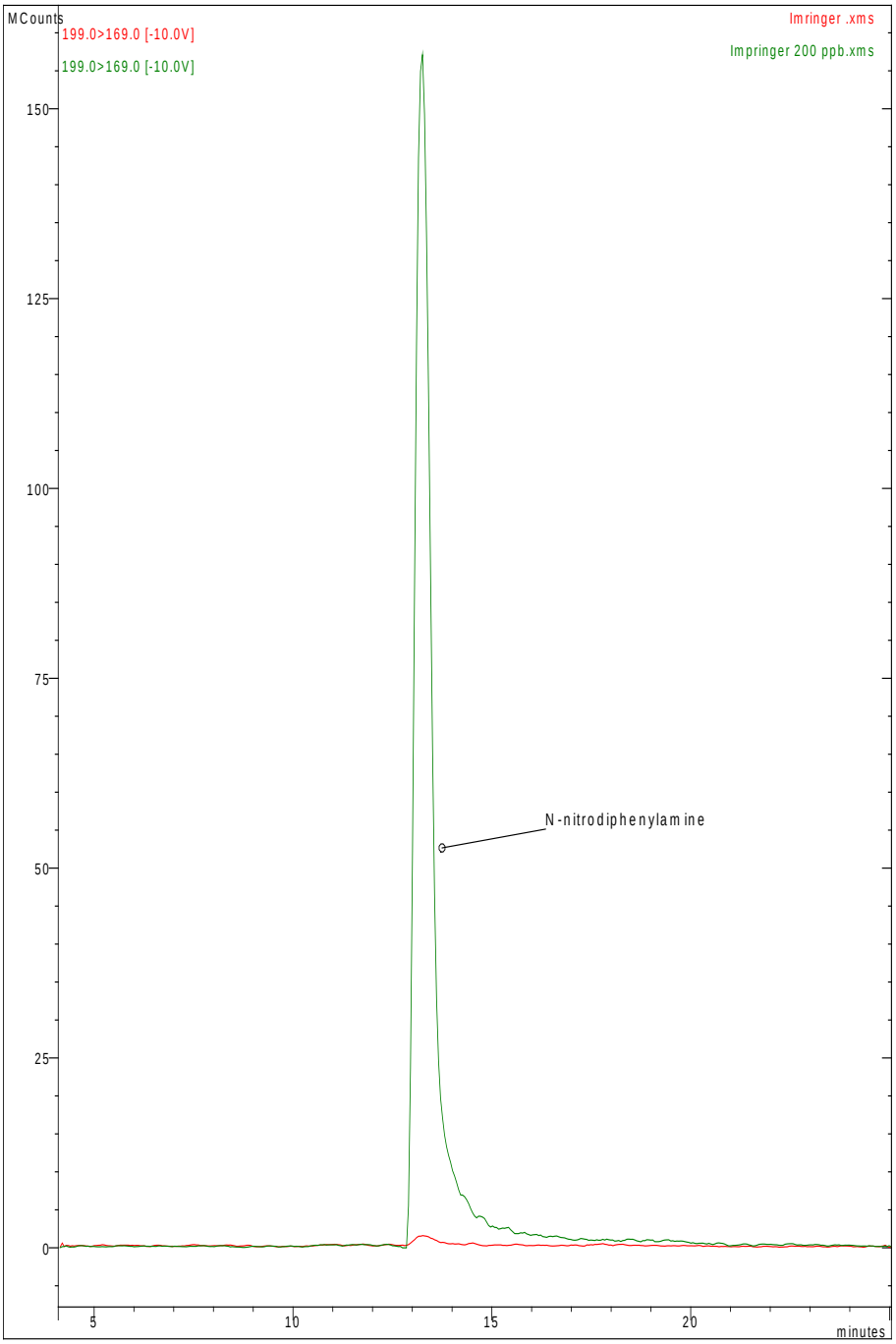


Figure 6.19. MRM for N-nitrosophenylamine in impinger solution and the spike at 200 ppb

7. DETERMINATION BY LC-MS-MS OF ALDEHYDES IN SOLVENTS AND WATERS

Title: Determination by LC-MS-MS of aldehydes in solvents and waters

Authors: Advanced Analytical Australia Pty Ltd (specifically, Rama Nimmagadda)

Scope: This method is for the determination of total formaldehyde and acetaldehyde in wash waters, impinger traps and PCC liquors.

Summary: The aldehydes are trapped or extracted with an acid solution of DNPH and the derivatised aldehydes are back extracted with a suitable solvent and determined by LC-MS-MS. In the report for job A11-0781, Dr Nimmagadda states (note that some formatting has been changed):

7.1. Introduction

A new method using liquid chromatography coupled with tandem mass spectrometry (LC-MS-MS) was developed to analyse aldehydes-dinitrophenyl hydrazine compleses (DNPH). A reversed phase column was used to separate aldehyde-DNPH complexes by liquid chromatography. Once separated by HPLC, aldehydes were ionised using electrospray and were detected on a triple quadrople mass spectrometer. Multiple reaction monitoring (MRM) was set up by infusing standard solutions of formaldehyde and acetaldehyde DNPH complexes (Table 7.1). The chromatograms for each individual MRM trasition for each of the aldehydes are presented in Figure 7.1. Atrazine-d5 was used as an internal standard for screening purpose. The sample descriptions are listed in Table 7.2.

Table 7.1. MRM transitions were set up for the following compounds:

Analyte	MRM Transition 1 Quantifier	MRM Transition 2 Qualifier
Formaldehyde-DNPH	209.0 ->133.0	209.0 -> 178.5
Acetaldehyde-DNPH	223.0 ->151.0	223.0 -> 163.0

Table 7.2. Sample description

A11-0781-17	Test 2: Impinger 1 spiked
A11-0781-18	Test 2: Impinger 2
A11-0781-19	Test 2: Impinger 3
A11-0781-20	Test 2: Impinger 4

7.2. Preliminary investigation of solvents

Initially, samples were analysed by concentrating 10 mL of the sample diluted 50 mL with DI (de-ionized) water and passed through solid phase extraction (SPE) cartridge. Hydrophilic-Lipophilic Balance Sorbent (HLB) solid phase cartridges were used to extract these solutions. Prior to loading the sample on SPE, the cartridge was conditioned with methanol and water. The cartridges were washed with water and allowed to dry for 5 min under vacuum. The aldehyde-DNPH complexes were eluted with methanol and concentrated to dryness under nitrogen. The samples were made up in 0.5 mL of mobile phase (30% methanol: 70% water + 0.1% formic acid). The standards were prepared by spiking 10 mL of 30% methanolamine solution and following the same procedure similar to that of samples. However, the samples, treated with 2,4-DNPH, had high background interference due to 2,4-DNPH compared to the standards.

At this stage, the samples were diluted 50 times by taking 20 µL iinto 2 mL vial and further makinig up the volume to 1 mL using mobile phase (30% methanol: 70% water + 0.1% formic acid). There were two sets of standards prepared ; one set of standards using DI water and other set of standards using blank 2,4-DNPH solution. The blank DI water did not contain any background interference. The 2,4 DNPH balnk solution has been detected for formaldehyde and acetaldehyde DNPH complexes. The intial limit of detection of 100 µg/L in methanolamine solutions, free of DNPH, could not be achieved in the solutions containg 2,4-DNPH due to high background matrix. Hence, the limit of reporting for samples was raised to 1 mg/L. The samples were anlysed using the calibration standards prepared using sample 2,4-DNPH solution and the results for the samples were represented in Table 7.3. The sample A11-0781-19 was spiked at 20 ppm to calculate the recoveries listed in Table 7.3.

Table 7.3. Analysis of samples and recoveries.

Sample	Formaldehyde-DNPH (ppm)	Acetaldehyde-DNPH (ppm)
A11-0781-17	300	300
A11-0781-18	<1	<1
A11-0781-19	<1	<1
A11-0781-20	<1	<1
A11-0781-19MS	104%	105%

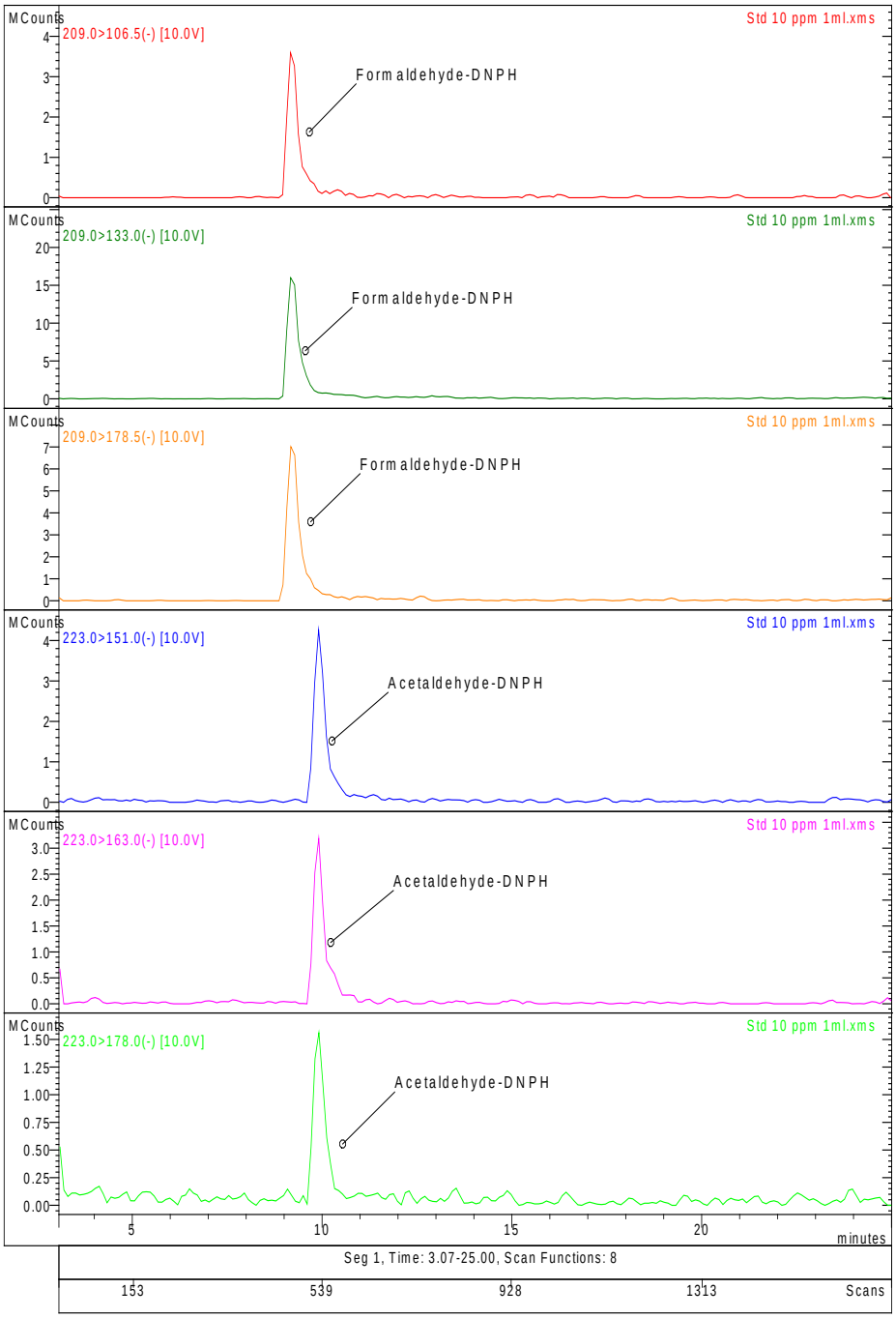


Figure 7.1. MRM transitions for formaldehyde-DNPH, acetaldehyde-DNPH and atrazine-d5 (internal standard).

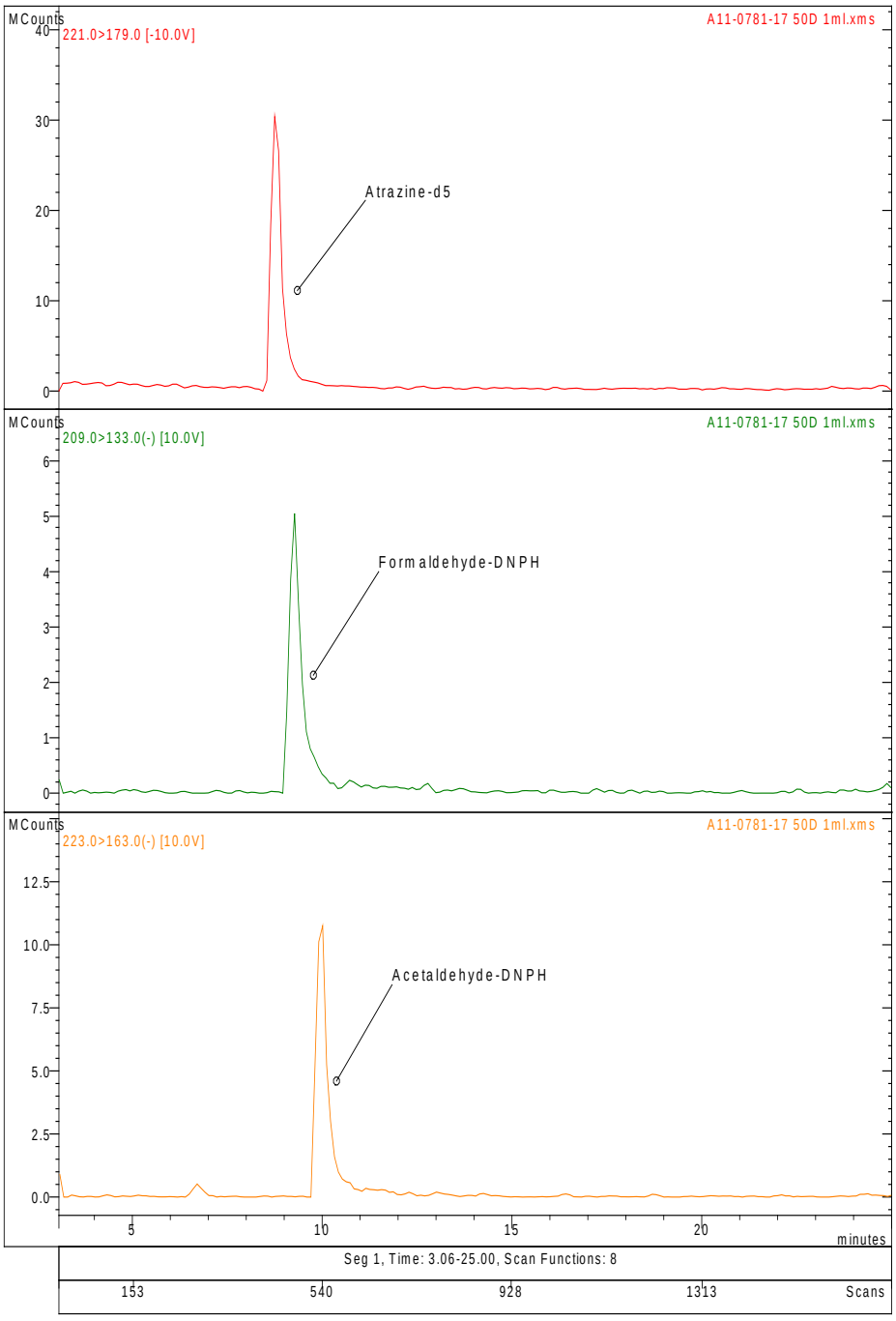


Figure 7.2. Chromatogram for A11-0781-17 sample diluted 50 times

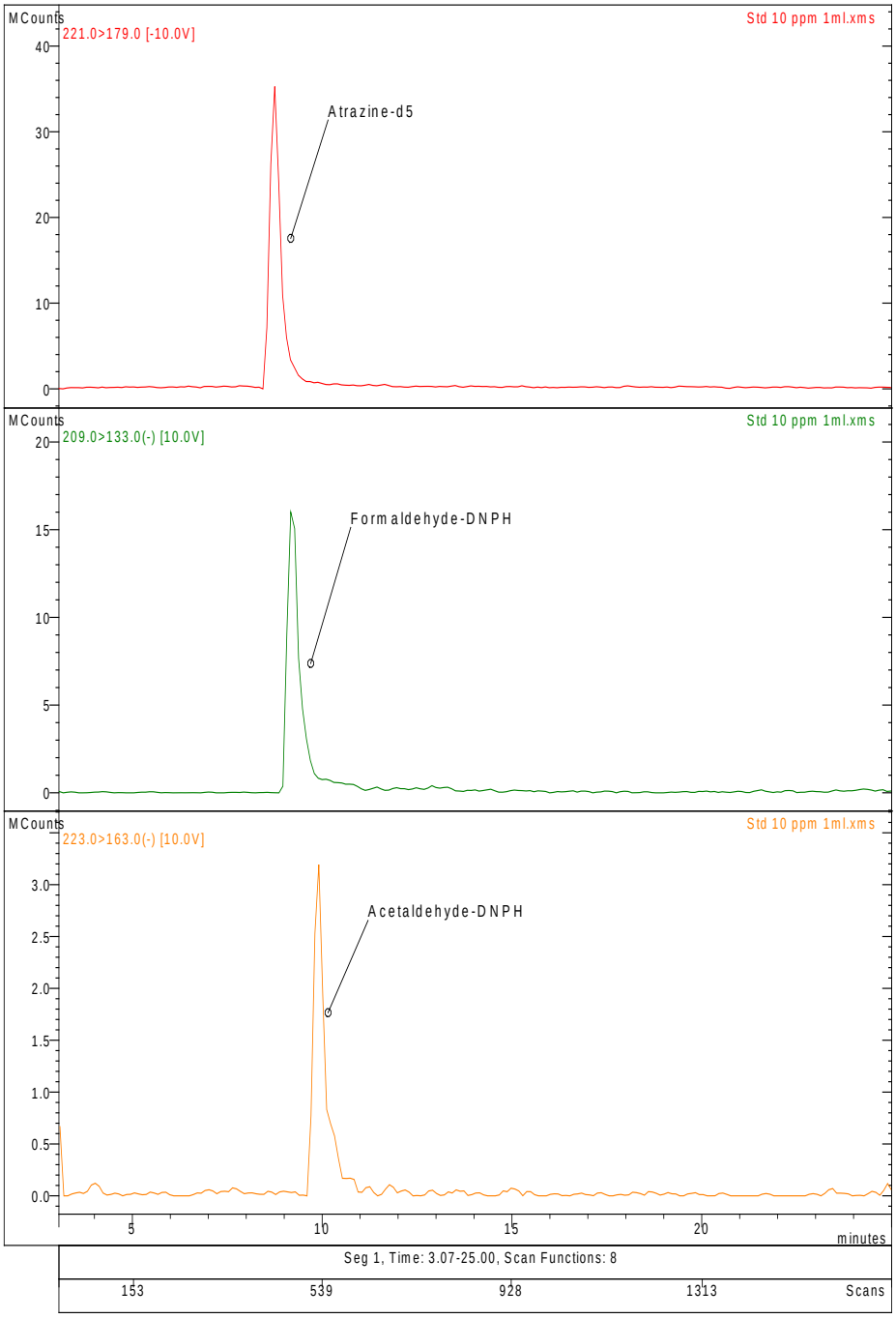


Figure 7.3. Chromatograms for Standards of 10 ppm

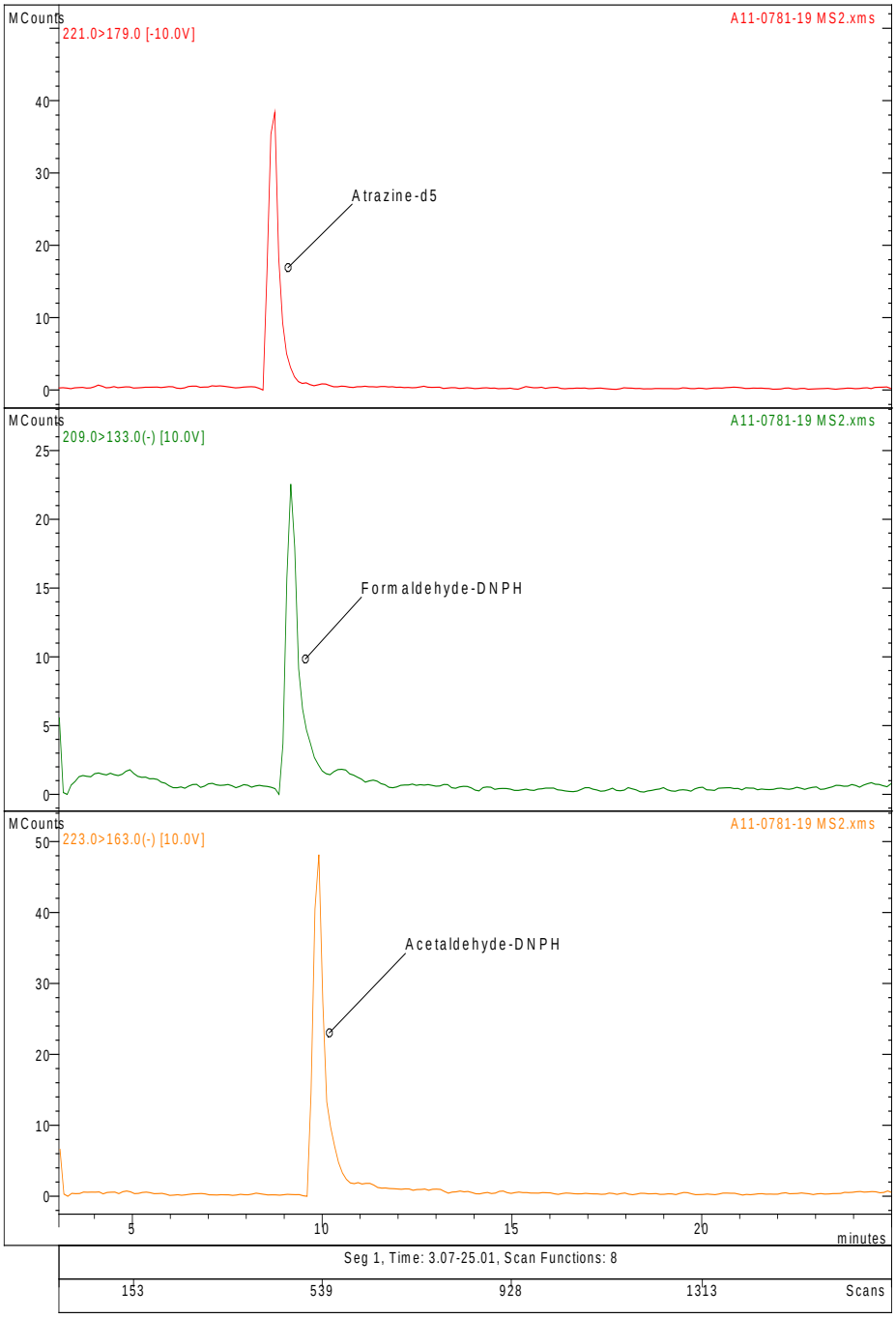


Figure 7.4. Chromatogram for spike on A11-0781-2MS

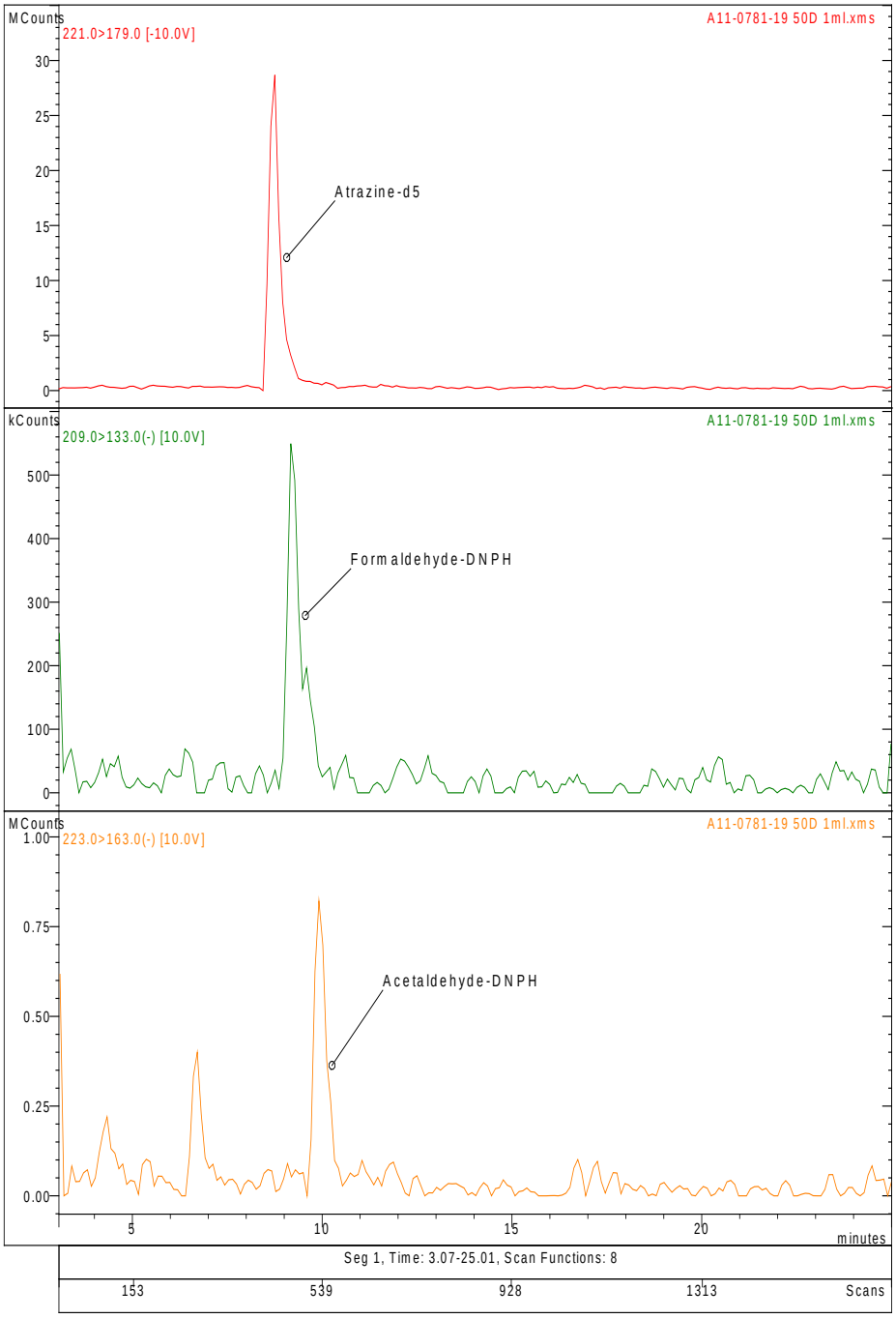


Figure 7.5. Chromatogram for spike on A11-0781-19

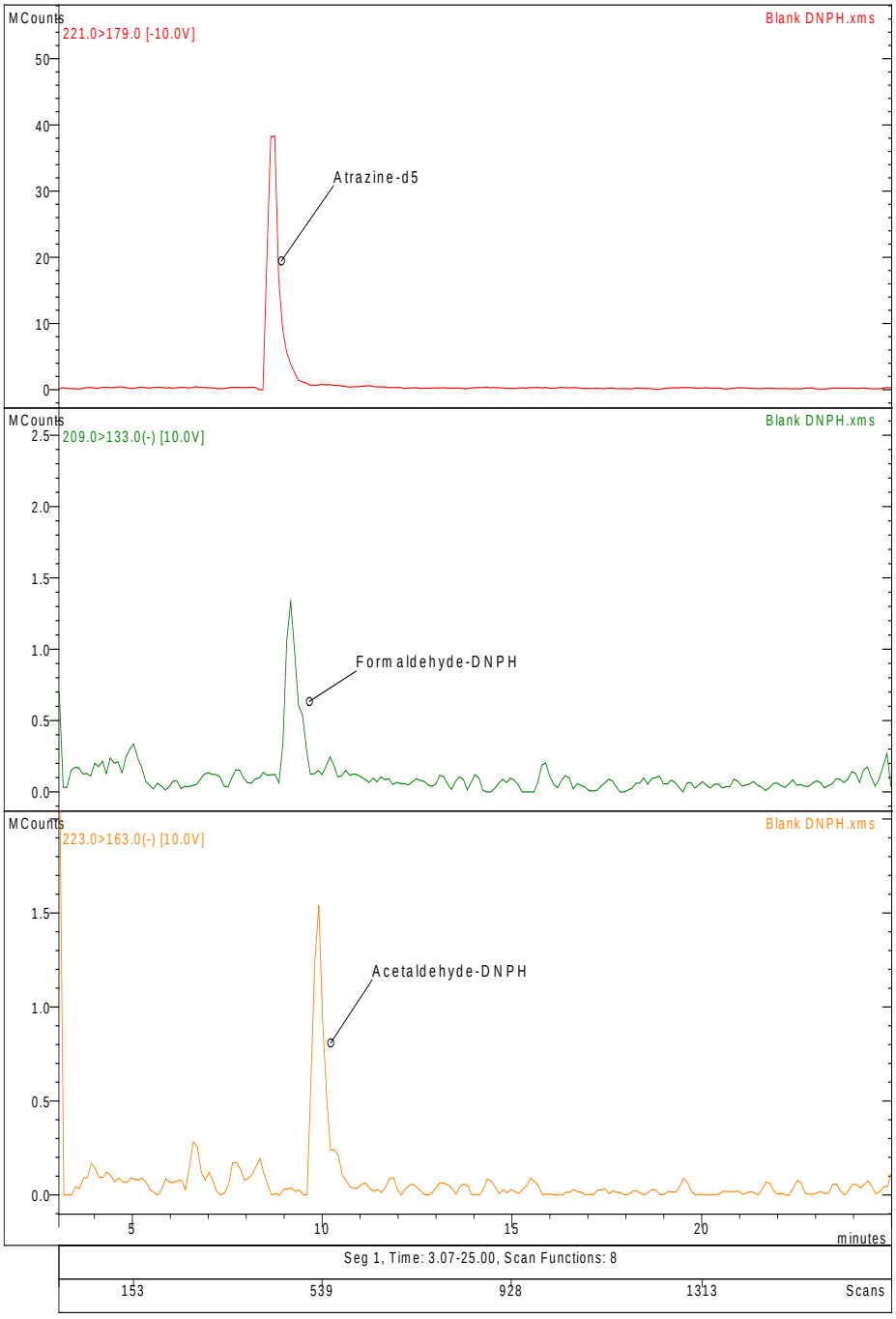


Figure 7.6. Chromatogram for Blank DNPH

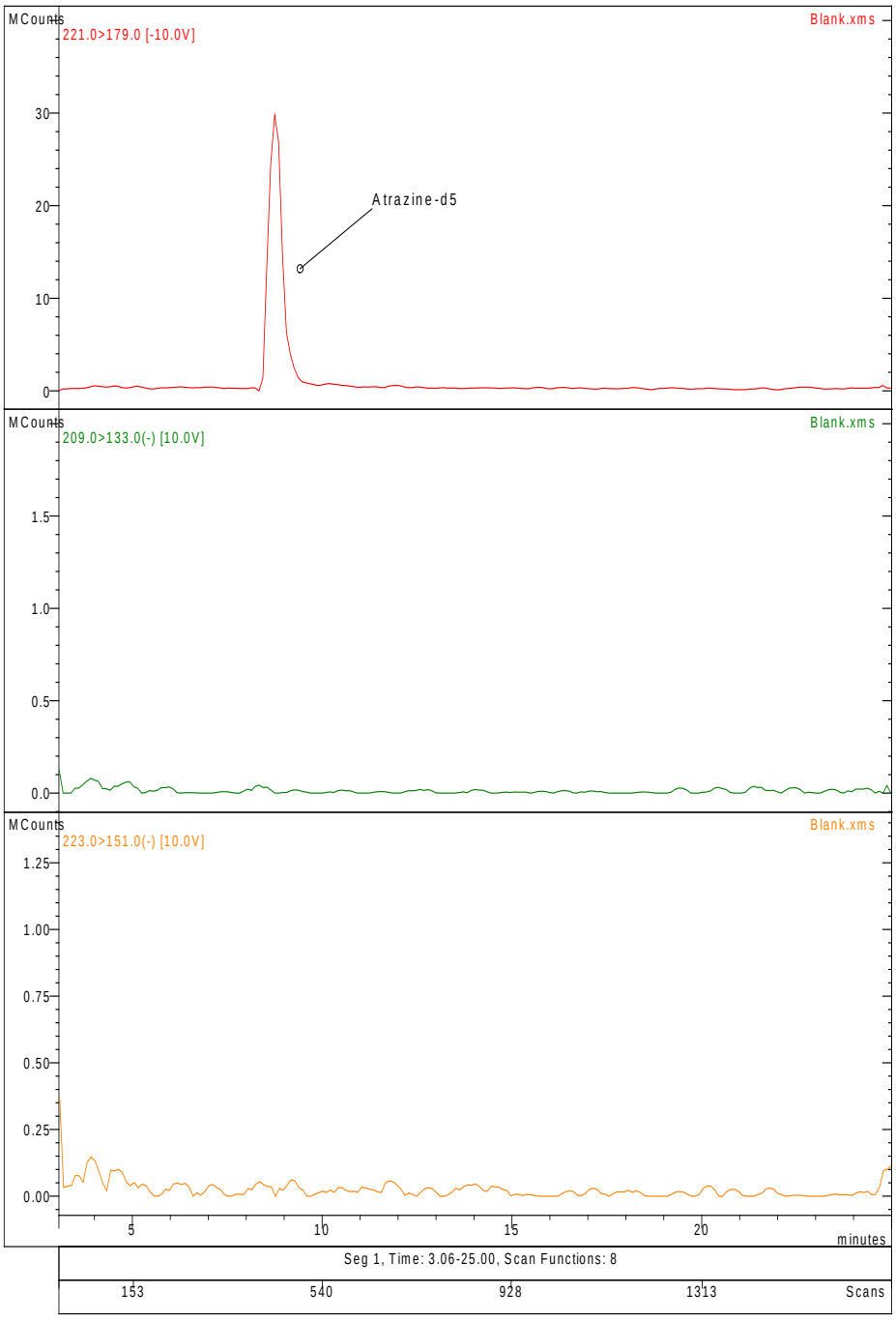


Figure 7.7. Chromatogram for Blank 30% methanolamine solution

8. DETERMINATION BY GC-MS OF AMIDES IN SOLVENTS AND WATERS

Title: Determination by GC-MS of amides in solvents and waters

Authors: Advanced Analytical Australia Pty Ltd (specifically Dr Mark Lewin)

Scope: This method is for the determination of formamide and acetamide in wash waters, impinger traps and PCC liquors.

Summary: The amides are extracted and determined by GC-MS.

The following report was drafted by Mark Lewin:

Preliminary Investigation of the Determination of Amines and Amides in 3%MEA Solutions

Report No: A11/1418
Report for CSIRO
Prepared by Dr Mark Lewin
Friday 15th April, 2011

Summary

Preliminary work for the determination of amines and amides in a 3% monoethanolamine (MEA) solution was performed. Formamide and acetamide are estimated to have a limit of quantitation of 0.1 mg/L. Dimethylamine, diethylamine, ethylamine, and propylamine were detected but did not chromatograph well and would require further investigation to determine optimum analytical conditions and limits of quantitation. Methylamine was not detected in this investigation

Standard Preparation

Neat standards of formamide, acetamide, diethylamine, and propylamine, and solutions of methylamine (40%), ethylamine (70%), and dimethylamine (40%) were used to prepare individual stocks in water at approximately 1000mg/L. The individual stocks were used to prepare a mixed solution containing each compound at 10mg/L, in 3% monoethanolamine. The 10mg/L solution in 3% MEA was then taken for analysis.

Analysis

Analysis was performed using an Agilent 7890A gas chromatograph fitted with a PTV inlet and an Agilent 5975C mass selective detector. A Varian VF-WAXms 30m×0.25mm×0.25µm capillary column was installed in the gas chromatograph. The PTV inlet was configured to perform a cold split injection. The mass selective detector was configured to record in full scan mode.

The chromatography and sensitivity of acetamide and formamide were both acceptable. Based on the signal-to-noise ratio for each of these compounds, it is estimated that the limit of quantitation

under the analytical conditions would be approximately 0.1mg/L if the mass selective detector was configured to record in selected ion monitoring (SIM) mode.

The chromatography and sensitivity for dimethylamine, diethylamine, ethylamine, and propylamine was poor due to co-elution with water. Under these analytical conditions, the limit of quantitiation is estimated to be 10-20mg/L. It is recommended that further optimisation be performed for these compounds prior to analysis.

Signed
Dr Mark Lewin
R&D Chemist
Advanced Analytical Australia

Note that the total report is in Appendix 3

9. DETERMINATION BY GC-MS OF ALKYLAMINES IN SOLVENTS AND WATERS (ADVANCED ANALYTICAL AUSTRALIA PTY LTD)

Title: Determination by GC-MS of amines in solvents and waters

Authors: Advanced Analytical Australia Pty Ltd

Scope: This method is for the determination of the volatile alkylamines in wash waters, impinger traps and PCC liquors.

Summary: The akylamines are derivatised with trifluoro acetic anhydride, extracted and determined by GC-MS.

See previous report by Dr Mark Lewin.

10. DETERMINATION BY GC-MS OF ALKYLAMINES IN SOLVENTS AND WATERS (ASUREQUALITY, NZ)

Title: Determination by GC-MS of volatile akylamines in solvents and waters

Authors: AsureQuality, NZ (specifically, Cliff Randall)

Scope: This method by GC-MS is for the determination of the volatile alkylamines in wash waters and PCC liquors.

Summary: The alkylamines are purged and extracted from the headspace and determined by GC-MS.

Advice from the analytical chemist, who was responsible for the determination of the volatile amines at AsureQuality is that: “Because the volatile amine analysis was a one-off non routine analysis I do not have measurement of uncertainty values. However I did run 4 water matrix spikes with the sample batch to enable the calculation of CV (coefficient of variance) and recovery/bias, which are as follows” (see Table 10.1):

Table 10.1. Statistics on four runs using water as a matrix

Analyte	Recovery %	Spike Level (ppm)	CV %
methylamine	90	150	9.0
ethylamine	101	50	7.8
diethylamine	101	5	5.8

“Unfortunately the recovery of the volatile amine for randomly spiked samples was quite variable. This variability suggests some sort of sample interaction with the amines? Of note was that there was a big difference in the colour of the samples even with those of the same composition”. The results for all samples are listed in Table 9.2:

Table 10.2. Results for volatile alkylamines obtained in solvent and wash down- water samples

Analyte	Concentration (ppm or mg/L)
methylamine	<15
ethylamine	<5
diethylamine	<0.5

Advice from Phil Bridgen of AsureQuality is: “Please note the specific comments below:

- No dimethylamine standard was available for the amine analysis but the appropriate mass spectral ions were monitored and no dimethylamine was detected in any of the samples. It is probable that the response for dimethylamine would be similar to ethylamine. (We are still hoping to obtain this standard for any future tests).
- Results have not been corrected for recoveries.
- Several matrix spike samples were analysed with these samples. The recoveries of these matrix spike samples has also been provided for your reference.” The results of the analyses are included in Appendix 4.

The advice from Dr Cliff Randall on the methodology used is:

“Volatile Amine Analysis

Method Reference: C Maris et al, "Static headspace analysis of aliphatic amines in aqueous samples", J Chrom A 846, 331-339

Procedure

1. 4.2-4.3 g NaCl into 20 mL vial
2. Add 10 ml deionised water for recovery standards or 10 mL sample
3. Add 1 mL 40% NaOH
4. Immediately cap and shake
5. Add amine spiking standard through septum for recovery standards and matrix spikes

Headspace

The sample was incubated at 80 ºC for 15 minutes on an Atas Focus Combi PAL autosampler and 0.5 mL of headspace analysed by GC-MS.

GC-MS

GC-MS analysis carried out on an Agilent 6890 GC with an Agilent 5973 MS. The GC column was a 60m 1.0 µm Zebron ZB5.”

11. DETERMINATION BY GC-MS-MS OF N-NITROSAMINES IN SOLVENTS AND WATERS

Title: Determination by GC-MS-MS of N-nitrosamines in solvents and waters

Authors: AsureQuality, NZ (in particular, Phil Brigden and Lorna Rolston)

Scope: This method by high resolution GC-MS-MS is for the determination of the N-nitrosoamines in wash waters and PCC liquors.

Summary: The N-nitrosamines are extracted and determined by high resolution GC-MS-MS.

A diluted aliquot of sample was used; this was fortified with an internal standard solution and extracted via SPE using a coconut charcoal cartridge. The analytes were eluted with organic solvent and analysed on a GC-HRMS using positive EI at 10,000 resolution. The sample concentrations were calculated from their relative responses against a 5-point standard calibration curve.

Advice from Phil Bridgen states that:
“The first analysis of the samples gave similar values for the EPA 521 mix (approx 0.5-0.7 mg/L) and a somewhat lower value for NMOR (~13 mg/L). The data from the first set was not used because the levels in the samples, being higher than anticipated, were impacting the associated batch QA samples (i.e. the very large responses from the samples were impacting on the comparatively low spikes) and the response for NMOR was far outside the calibration range (the difference in NMOR data from the first and second analysis was attributed to this latter point). Therefore, analysis of the samples was repeated, taking a smaller aliquot to bring the levels within the working calibration range. The data for the second (repeat) analysis was used for reporting purposes.

The calculations for the reported data have been checked, with no errors found. The data for the matrix spike associated with the reported samples was within method specifications. It is also considered that the data from the second and first analysis are in reasonable agreement. As such, AsureQualtiy cannot find any evidence for concern of the values obtained from the analysis of the samples.

The uncertainty of measurement for each analyte below (95% confidence level) is:
NDMA = 11%
NMEA = 32%
NDEA = 67%
NDPA = 18%
NPIP = 7.7%
NMOR = 62%
NPYR = 13%

Note - these uncertainties were obtained by replicate analyses of distilled water samples spiked at a level of 1 ng/L for each nitrosamine. The higher uncertainties for NDEA and NMOR are attributed to background levels of these analytes being observed near the spiked level.

Regarding the reported internal standard recoveries, generally this batch of samples returned recoveries in the range of ~40-60%. The internal standards are added to the sample before

extraction, and the recovery reported is an absolute recovery of the internal standards from the entire analytical process. As the nitrosamine analytes are quantified against the response of the internal standards, the reported nitrosamine levels are corrected for recoveries. Thus, there is not any particular concerns about low recoveries, even at 35%. Note the matrix spike for this batch also had internal standard recoveries between 44 and 55%, but still returned recoveries of the native nitrosamine analytes between 90 and 114%."

The results are listed in appendix 5. It should be noted that all the volatile nitrosamines are at extremely low concentrations in the samples of MEA solvents and wash waters.

Note also that the in Appendix 5, the report identified as "84132 Nitrosamine Certificate.pdf" contains the results of spiked MEA supplied to AsureQuality by CSIRO.

APPENDIX 1: CONDENSED VERSION OF QUANTITATIVE METHOD FOR DETERMINATION OF N-NITROSODIETHANOLAMINE

A1.1 Title. Quantitative method for NDELA (N-nitrosodiethanolamine) in aqueous post-combustion capture matrix using IC-MRM

A1.2 Authors. P. Jackson and M.I. Attalla

A1.3 Method. This method applies to waters, wash-waters or PCC liquors with the following caveat. A portion of typical 300 mg/g PCC liquor (test sample) shall be diluted using charcoal-filtered water (R > 18 MΩ) by a factor of at least 1/20, preferably by 1/40-1/100. This is done to avoid a reduction in sensitivity arising from MEA as described in A.3 Introduction. Suspended solids should be removed from any test sample using pelletization (e.g. by low speed centrifugation), prior to dilution. Test portions of water- and wash-water samples can be analysed without dilution after centrifugation.

A1.4 Experimental Conditions.

Test sample injection volume: 40 μl
Instrumentation: LC-MS/MS (Waters Acquity MS^2)
Ion mode: Positive ion electrospray
MS operation mode: multiple reaction monitoring (MRM)
Capillary voltage: 3.57 kV
Cone voltage: 38 V
Extractor: 2.0 V
RF: 0.2 V
Source temperature: 150 °C
Desolvation temperature: 350 °C
Desolvation gas flow rate: 500 L/hr
Collision gas flow rate: 0.03 ml/min
Transition dwell time: 0.1 s
Interscan delay: 0.02 s
Inter-channel delay: 0.02 s
MS1 low mass resolution: 14.0
MS1 high mass resolution: 14.0
MS3 low mass resolution: 13.5
MS3 high mass resolution: 13.5
MS analyser baseline pressure: $< 1.3 \times 10^{-5}$ mbar
MS analyser pressure after admission of collision gas: $1.2\text{-}1.3 \times 10^{-3}$ mbar
Collision gas: high purity argon
T-cell bias: 12 V
Multiplier voltage: -645 V
Run time: 25 mins
Transitions:
(i) $135.1 \rightarrow 74.2$
(ii) $135.1 \rightarrow 104.1$
(iii) $135.1 \rightarrow 105.1$
Peak height or peak area used: Peak area
Smoothing prior to peak integration: Mean of 5 scans
Column: Dionex CS16 3×250 mm
Column temperature: 20 °C
Injection volume: 40 μl

Solvent flow rate: 0.3 ml/min
Mobile phases: A = 100 % MeCN (LC-MS grade, Sigma Aldrich), B = 1.2 % aqueous HCOOH (HCOOH, LC-MS grade, Sigma Aldrich)
Gradient:

Table A1.1. IC-MRM gradient conditions

Time (mins)	A %	B %
0.00	85.0	15.0
10.00	85.0	15.0
12.00	1.0	99.0
16.00	1.0	99.0
18.00	99.0	1.0
22.00	99.0	1.0
23.00	85.0	15.0
25.00	85.0	15.0

APPENDIX 2: CONDENSED VERSION OF QUANTITATIVE METHOD FOR DETERMINATION OF N-NITROSOPIPERAZINE

A2.1 Title. Quantitative method for NPZ (N-nitrosopiperazine) in aqueous solutions using reversed-phase HPLC-MS/MS

A2.2 Authors. P. Jackson and M.I. Attalla

A2.3 Method. Due to the presence of an underivatized secondary nitrogen centre in NPz, ion-pairing with matrix components is problematical during analyte measurement. It also renders separation of the analyte from the matrix almost impossible using wet-chemical or chromatographic techniques. At a concentration of 4.84 ppm NPz and 120 ppm loaded Pz, 99 % of the signal is suppressed. If the LOD in water represents the signal measured when there is 99 % suppression by loaded Pz, the following estimates of the detection limit pertaining to NPz in loaded solutions were determined for each transition (assuming the suppression effect is linear with [NPz]). For M/z 116 $\rightarrow$ 44, LOD = 5.1 ppm; M/z 116 $\rightarrow$ 85, LOD = 0.26 ppm; M/z 116 $\rightarrow$ 86, LOD = 0.60 ppm.
The maximum tolerable concentration of loaded Pz which can be present with NPz before complete signal suppression has also been approximated: for M/z 116 $\rightarrow$ 44, [Pz] = 112 ppm; M/z 116 $\rightarrow$ 85, [Pz] = 213 ppm; M/z 116 $\rightarrow$ 86, [Pz] = 174 ppm. These values assume [Pz] is not limiting. Due to the strong ion-pairing nature of the analyte, it is recommended that this method is only applied to wash- and discharge waters when [Pz] < 150 ppm (for detection only), preferably when [Pz] < 100 ppm.

A2.4 Experimental conditions

Test sample injection volume: 40 μl
Instrumentation: LC-MS/MS (Waters Acquity MS^2)
Ion mode: Positive ion electrospray
MS operation mode: multiple reaction monitoring (MRM)
Capillary voltage: 3.57 kV
Cone voltage: 20 V
Extractor: 2.0 V
RF: 0.2 V
Source temperature: 150 °C
Desolvation temperature: 350 °C
Desolvation gas flow rate: 500 L/hr
Collision gas flow rate: 0.03 ml/min
Transition dwell time: 0.1 s
Interscan delay: 0.02 s
Inter-channel delay: 0.02 s
MS1 low mass resolution: 14.0
MS1 high mass resolution: 14.0
MS3 low mass resolution: 13.5
MS3 high mass resolution: 13.5
MS analyser baseline pressure: < 1.3×10^{-5} mbar
MS analyser pressure after admission of collision gas: 1.2-1.3 $\times 10^{-3}$ mbar
Collision gas: high purity argon
T-cell bias: 12 V
Multiplier voltage: -645 V
Run time: 25 mins
Transitions:
(i) 116.1 $\rightarrow$ 44.1

(ii) 116.1 → 86.1
(iii) 116.1 → 85.1
Peak height or peak area used: Peak area
Smoothing prior to peak integration: Mean of 5 scans
Column: C18, 3.5 μm x (2.1 x 100) mm
Column temperature: 20 °C
Injection volume: 40 μl
Mobile phases: A = 100 % MeOH (LC-MS grade, Sigma Aldrich), B = charcoal-filtered water
Gradient:

Table A2.1 HPLC-MS/MS gradient conditions

Time (mins)	A %	B %	Flow rate (ml/min)
0.00	50.0	50.0	0.500
8.00	50.0	50.0	0.500
15.00	98.0	2.0	0.500
16.00	98.0	2.0	1.000
18.50	98.0	2.0	1.000
19.00	2.0	98.0	1.000
21.50	2.0	98.0	1.000
22.00	50.0	50.0	0.500

APPENDIX 3: REPORT FROM DR LEWIN OF ADVANCED ANALYTICAL AUSTRALIA PTY LTD

ADVANCED ANALYTICAL AUSTRALIA

Preliminary Investigation of the Determination of Amines and Amides in 3%MEA Solutions

Report No: A11/1418

Report for CSIRO

Prepared by Dr Mark Lewin

Friday 15th April, 2011

Summary

Preliminary work for the determination of amines and amides in a 3% monoethanolamine (MEA) solution was performed. Formamide and acetamide are estimated to have a limit of quantitation of 0.1 mg/L. Dimethylamine, diethylamine, ethylamine, and propylamine were detected but did not chromatograph well and would require further investigation to determine optimum analytical conditions and limits of quantitation. Methylamine was not detected in this investigation

Standard Preparation

Neat standards of formamide, acetamide, diethylamine, and propylamine, and solutions of methylamine (40%), ethylamine (70%), and dimethylamine (40%) were used to prepare individual stocks in water at approximately 1000mg/L. The individual stocks were used to prepare a mixed solution containing each compound at 10mg/L, in 3% monoethanolamine. The 10mg/L solution in 3% MEA was then taken for analysis.

Analysis

Analysis was performed using an Agilent 7890A gas chromatograph fitted with a PTV inlet and an Agilent 5975C mass selective detector. A Varian VF-WAXms 30m×0.25mm×0.25µm capillary column was installed in the gas chromatograph. The PTV inlet was configured to perform a cold split injection. The mass selective detector was configured to record in full scan mode.

The chromatography and sensitivity of acetamide and formamide were both acceptable. Based on the signal-to-noise ratio for each of these compounds, it is estimated that the limit of quantitation under the analytical conditions would be approximately 0.1mg/L if the mass selective detector was configured to record in selected ion monitoring (SIM) mode.

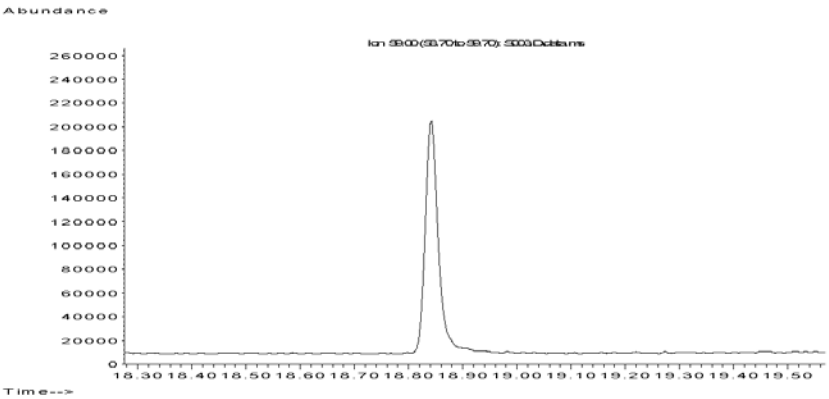


Figure 1: Extracted ion chromatogram (Ion 44) for 10mg/L acetamide in 3% MEA.

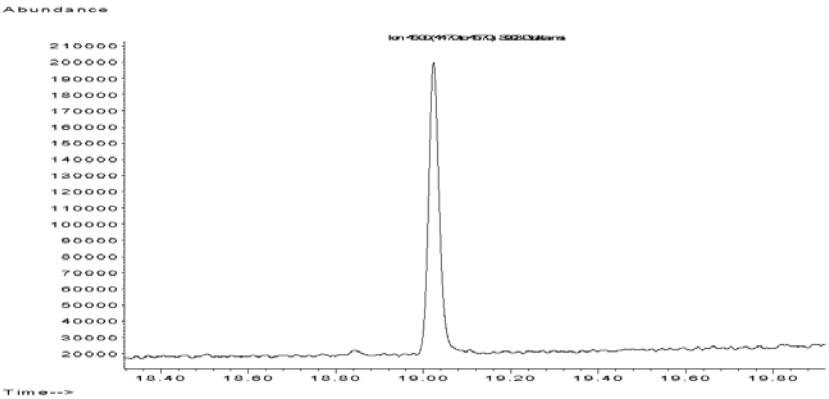


Figure 2: Extracted ion chromatogram (Ion 45) for 10mg/L formamide in 3% MEA.

The chromatography and sensitivity for dimethylamine, diethylamine, ethylamine, and propylamine was poor due to co-elution with water. Under these analytical conditions, the limit of quantitiation is estimated to be 10-20mg/L. It is recommended that further optimisation be performed for these compounds prior to analysis.

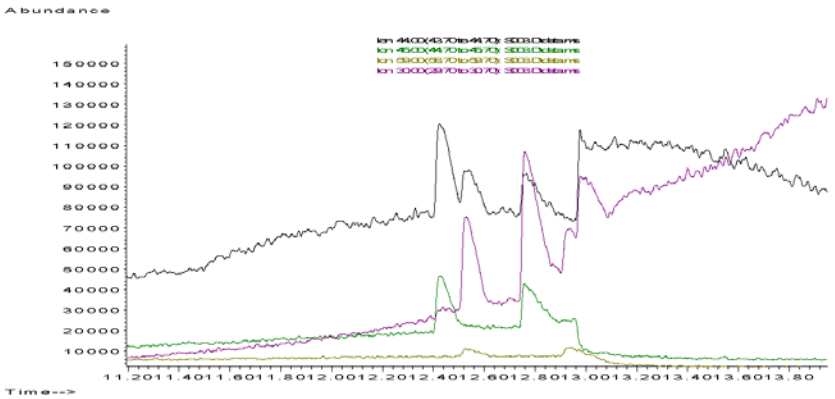


Figure 3: Extracted ion chromatograms (Ions 44, 45, 59, and 30) showing the poor chromatography and sensitivity for dimethylamine, diethylamine, ethylamine, and propylamine.

Methylamine was not detected under these analytical conditions. Further investigation to find suitable conditions is required to determine a limit of quantitation for methylamine.

Dr Mark Lewin
R&D Chemist
Advanced Analytical Australia

APPENDIX 4: CERTIFICATE OF ANALYSIS FOR VOLATILE AMINES

AsureQuality

1C Quadrant Drive, Waiwhetu
P.O. Box 31 242,
Lower Hutt 5010, New Zealand

T 64 4 5708800
F 64 4 5708176
W www.asurequality.com

Certificate of Analysis

Date Issued: 18-Mar-11

Client: CSIRO Energy Technology
P O Box 52
North Ryde 1670
AUSTRALIA

Attention: Ken Riley

Date Received: 22-Feb-11

AsureQuality Lab. Reference: 89565

Sample Type: Water

Analysis: **Volatile amines in water**

Method:

The sample was analysed by headspace gas chromatography - mass spectrometry.

Results are reported to two significant figures in milligrams per litre (mg/L), equivalent to ppm, on an as received basis. Detection limits are reported to one significant figure.

Unless requested, samples will be disposed of eight weeks from the date of this report.

Comments:

Dr. Cliff Randall
Senior Scientist
AsureQuality Limited

Results: Volatile amines in water

Sample Identification: A 30-40% MEA in water
Laboratory Reference: 89565-1

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: B 30-40% MEA in water
Laboratory Reference: 89565-2

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: C 30-40% MEA in water
Laboratory Reference: 89565-3

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: D 30-40% MEA in water
Laboratory Reference: 89565-4

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: E 30-40% MEA in water
Laboratory Reference: 89565-5

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: F Plant wash water 1-3% MEA
Laboratory Reference: 89565-6

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: G Plant wash water 1-3% MEA
Laboratory Reference: 89565-7

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: H Plant wash water 1-3% MEA
Laboratory Reference: 89565-8

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: I Plant wash water 1-3% MEA
Laboratory Reference: 89565-9

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: J Plant wash water 1-3% MEA
Laboratory Reference: 89565-10

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: M 30-40% MEA in water
Laboratory Reference: 89565-11

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: N 30-40% MEA in water
Laboratory Reference: 89565-12

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: O 30-40% MEA in water
Laboratory Reference: 89565-13

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: P 30-40% MEA in water
Laboratory Reference: 89565-14

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: Q 30-40% MEA in water
Laboratory Reference: 89565-15

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: Rich Liquor 30-40% MEA in water
Laboratory Reference: 89565-16

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: Lean Liquor 30-40% MEA in water
Laboratory Reference: 89565-17

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: 451 30-40% MEA in water
Laboratory Reference: 89565-18

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: 510 30-40% MEA in water
Laboratory Reference: 89565-19

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: 512 30-40% MEA in water
Laboratory Reference: 89565-20

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are reported on an as received basis and are not corrected for recoveries.
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: Laboratory Blank
Laboratory Reference: 89565-BLANK

Date Received: Not Applicable
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Level.† (mg/L)
methylamine	< 15
ethylamine	< 5
diethylamine	< 0.5

† = Results are calculated using the average volume of samples in this batch
< = Less than limit of detection.

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: C 30-40% MEA in water
Laboratory Reference: 89565-3 Matrix Spike

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Spiked Level (mg/L)	Recovered (mg/L)
methylamine	150	53
ethylamine	50	18
diethylamine	5.0	1.1

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: D 30-40% MEA in water
Laboratory Reference: 89565-4 Matrix Spike

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Spiked Level (mg/L)	Recovered (mg/L)
methylamine	150	100
ethylamine	50	34
diethylamine	5.0	2.3

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: F Plant wash water 1-3% MEA
Laboratory Reference: 89565-6 Matrix Spike

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Spiked Level (mg/L)	Recovered (mg/L)
methylamine	150	130
ethylamine	50	47
diethylamine	5.0	5.1

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: P 30-40% MEA in water
Laboratory Reference: 89565-14 Matrix Spike

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Spiked Level (mg/L)	Recovered (mg/L)
methylamine	150	47
ethylamine	50	17
diethylamine	5.0	0.82

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: Rich Liquor 30-40% MEA in water
Laboratory Reference: 89565-16 Matrix Spike

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Spiked Level (mg/L)	Recovered (mg/L)
methylamine	150	15
ethylamine	50	7.4
diethylamine	5.0	0.33

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

Results: Volatile amines in water

Sample Identification: 512 30-40% MEA in water
Laboratory Reference: 89565-20 Matrix Spike

Date Received: 22-Feb-2011
Date Extracted: 16-Mar-2011
Date Analysed: 16-Mar-2011

Analyte	Spiked Level (mg/L)	Recovered (mg/L)
methylamine	150	13
ethylamine	50	7.7
diethylamine	5.0	0.26

Lab Analyst: CJR Data Analyst: CJR Authorised: Cliff Randall

APPENDIX 5: CERTIFICATES OF ANALYSIS FOR NITROSAMINES

17 March 2011

AsureQuality

1C Quadrant Drive, Gracefield
P.O. Box 31 242, Lower Hutt
Wellington, New Zealand

T 64 4 5708800
F 64 4 5708176
W www.asurequality.com

Certificate of Analysis

Date Issued: 17 March 2011

Client: CSIRO Energy Technology
West Entrance, Riverside Corporate Park, Delhi Rd
West Ryde
NSW, 2113
Australia

Attention: Ken Riley

AsureQuality Lab. Reference: 89565

Sample Type(s): Aqueous

Analysis: **Nitrosamines**

Method: In-House HRGC-HRMS Method (Isotope Dilution)

Results are reported in milligrams per litre (mg/L), equivalent to ppm, on an as received basis to three significant figures. The DL value is reported to three significant figures. Results have been corrected for recoveries.

Unless requested otherwise, samples will be disposed of three months from the date of this report.

Comments:
None.

Phil Bridgen
Scientist
AsureQuality Limited

ilac-MRA 131 new zealand accredited laboratory

Results: Nitrosamines

Laboratory Reference: **89565-1**

Sample Identification: **A 30-40% MEA in water**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 14 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.00810		64	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00380			
N-nitrosodiethylamine (NDEA)	0.0322		70	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00705	74	50 - 150	
N-nitrosopiperidine (NPIP)	0.00320				
N-nitrosomorpholine (NMOR)	ND	0.0300			
N-nitrosopyrrolidine (NPYR)	ND	0.00365			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-2**

Sample Identification: **B 30-40% MEA in water**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 14 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.00630		58	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00410			
N-nitrosodiethylamine (NDEA)	0.00800		64	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00715	64	50 - 150	
N-nitrosopiperidine (NPIP)	0.00250				
N-nitrosomorpholine (NMOR)	ND	0.0363			
N-nitrosopyrrolidine (NPYR)	ND	0.00440			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-3**

Sample Identification: **C 30-40% MEA in water**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 14 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.00650		54	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00350			
N-nitrosodiethylamine (NDEA)	0.0130		57	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00710	63	50 - 150	
N-nitrosopiperidine (NPIP)	0.00285				
N-nitrosomorpholine (NMOR)	ND	0.0286			
N-nitrosopyrrolidine (NPYR)	ND	0.00330			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-4**

Sample Identification: **D 30-40% MEA in water**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 14 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.00715		54	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00440			
N-nitrosodiethylamine (NDEA)	0.00825		58	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00685	64	50 - 150	
N-nitrosopiperidine (NPIP)	0.00280				
N-nitrosomorpholine (NMOR)	ND	0.0362			
N-nitrosopyrrolidine (NPYR)	ND	0.00455			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-5**

Sample Identification: **E 30-40% MEA in water**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 14 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.00890		56	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00355			
N-nitrosodiethylamine (NDEA)	0.0175		61	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00565	69	50 - 150	
N-nitrosopiperidine (NPIP)	0.00250				
N-nitrosomorpholine (NMOR)	ND	0.0270			
N-nitrosopyrrolidine (NPYR)	ND	0.00320			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-6**

Sample Identification: **F Plant wash water 1 - 3 % MEA**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 14 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.00935		52	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00345			
N-nitrosodiethylamine (NDEA)	0.00595		59	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00715	65	50 - 150	
N-nitrosopiperidine (NPIP)	0.00240				
N-nitrosomorpholine (NMOR)	ND	0.0300			
N-nitrosopyrrolidine (NPYR)	ND	0.00345			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

F: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-7**

Sample Identification: **G Plant wash water 1 - 3 % MEA**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 14 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.00800		55	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00415			
N-nitrosodiethylamine (NDEA)	0.00570		55	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00735	60	50 - 150	
N-nitrosopiperidine (NPIP)	0.00230				
N-nitrosomorpholine (NMOR)	ND	0.0352			
N-nitrosopyrrolidine (NPYR)	ND	0.00430			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-BLA**

Sample Identification: **Laboratory Blank A (Applies to sample 89565-1 to -7)**

Date Received: Not Applicable

Date Extracted: 14 March 2011

Date Analysed: 16 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.00705		64	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00335			
N-nitrosodiethylamine (NDEA)	0.0136		71	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00550	74	50 - 150	
N-nitrosopiperidine (NPIP)	0.00315				
N-nitrosomorpholine (NMOR)	ND	0.0308			
N-nitrosopyrrolidine (NPYR)	ND	0.00390			

Footnotes:

[1] Results are calculated using the average weight of samples in this batch

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

17 March 2011

AsureQuality

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Certificate of Analysis

Date Issued: 17 March 2011

Client: CSIRO Energy Technology
West Entrance, Riverside Corporate Park, Delhi Rd
West Ryde
NSW, 2113
Australia

Attention: Ken Riley

AsureQuality Lab. Reference: 89565

Sample Type(s): Aqueous

Analysis: **Nitrosamines**
Method: In-House HRGC-HRMS Method (Isotope Dilution)

Results are reported in milligrams per litre (mg/L), equivalent to ppm, on an as received basis to three significant figures. The DL value is reported to three significant figures. Results have been corrected for recoveries.

Unless requested otherwise, samples will be disposed of three months from the date of this report.

Comments:
None.

Phil Bridgen
Scientist
AsureQuality Limited

ilac-MRA 131 laboratory

Results: Nitrosamines

Laboratory Reference: **89565-8**

Sample Identification: **H Plant wash water 1 - 3 % MEA**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 15 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.0101		64	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00435			
N-nitrosodiethylamine (NDEA)	0.00525		70	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00710	75	50 - 150	
N-nitrosopiperidine (NPIP)	0.00340				
N-nitrosomorpholine (NMOR)	ND	0.0364			
N-nitrosopyrrolidine (NPYR)	ND	0.00425			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

F: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-9**

Sample Identification: **I Plant wash water 1 - 3 % MEA**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 15 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.0109		67	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00550			
N-nitrosodiethylamine (NDEA)	0.00490		68	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00820	73	50 - 150	
N-nitrosopiperidine (NPIP)	0.00290				
N-nitrosomorpholine (NMOR)	ND	0.0414			
N-nitrosopyrrolidine (NPYR)	ND	0.00480			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-10**

Sample Identification: **J Plant wash water 1 - 3 % MEA**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 15 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.00935		72	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00365			
N-nitrosodiethylamine (NDEA)	0.00475		75	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00640	79	50 - 150	
N-nitrosopiperidine (NPIP)	0.00350				
N-nitrosomorpholine (NMOR)	ND	0.0320			
N-nitrosopyrrolidine (NPYR)	ND	0.00370			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

⚐: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-11**

Sample Identification: **M 30-40% MEA in water**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 15 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.0120		69	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00325			
N-nitrosodiethylamine (NDEA)	0.00815		71	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00575	72	50 - 150	
N-nitrosopiperidine (NPIP)	0.00325				
N-nitrosomorpholine (NMOR)	ND	0.0312			
N-nitrosopyrrolidine (NPYR)	ND	0.00385			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-12**

Sample Identification: **N 30-40% MEA in water**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 15 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.00995		64	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00345			
N-nitrosodiethylamine (NDEA)	0.00560		67	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00535	72	50 - 150	
N-nitrosopiperidine (NPIP)	0.00400				
N-nitrosomorpholine (NMOR)	ND	0.0288			
N-nitrosopyrrolidine (NPYR)	ND	0.00345			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-13**

Sample Identification: **O 30-40% MEA in water**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 15 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.00775		60	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00350			
N-nitrosodiethylamine (NDEA)	0.00415		62	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00525	65	50 - 150	
N-nitrosopiperidine (NPIP)	0.00375				
N-nitrosomorpholine (NMOR)	ND	0.0366			
N-nitrosopyrrolidine (NPYR)	ND	0.00420			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-BLB**

Sample Identification: **Laboratory Blank B (Applies to sample 89565-8 to -13)**

Date Received: Not Applicable

Date Analysed: 16 March 2011

Date Extracted: 15 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.00910		47	50 - 150	⚑
N-nitrosomethylethylamine (NMEA)	ND	0.00450			
N-nitrosodiethylamine (NDEA)	0.00685		47	50 - 150	⚑
N-nitrosodi-n-propylamine (NDPA)	ND	0.00760	51	50 - 150	
N-nitrosopiperidine (NPIP)	0.00360				
N-nitrosomorpholine (NMOR)	ND	0.0354			
N-nitrosopyrrolidine (NPYR)	ND	0.00435			

Footnotes:

[1] Results are calculated using the average weight of samples in this batch

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

⚑: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

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Certificate of Analysis

Date Issued: 18 March 2011

Client: CSIRO Energy Technology
West Entrance, Riverside Corporate Park, Delhi Rd
West Ryde
NSW, 2113
Australia

Attention: Ken Riley

AsureQuality Lab. Reference: 89565

Sample Type(s): Aqueous

Analysis: **Nitrosamines**

Method: In-House HRGC-HRMS Method (Isotope Dilution)

Results are reported in milligrams per litre (mg/L), equivalent to ppm, on an as received basis to three significant figures. The DL value is reported to three significant figures. Results have been corrected for recoveries.

Unless requested otherwise, samples will be disposed of three months from the date of this report.

Comments:
None.

Phil Bridgen
Scientist
AsureQuality Limited

ilac-MRA 131 new zealand accredited laboratory

Results: Nitrosamines

Laboratory Reference: **89565-14**

Sample Identification: **P 30-40% MEA in water**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 16 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.00985		66	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00375			
N-nitrosodiethylamine (NDEA)	0.00910		68	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00985	67	50 - 150	
N-nitrosopiperidine (NPIP)	0.00340				
N-nitrosomorpholine (NMOR)	ND	0.0352			
N-nitrosopyrrolidine (NPYR)	ND	0.00540			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-15**

Sample Identification: **Q 30-40% MEA in water**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 16 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.0119		63	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00415			
N-nitrosodiethylamine (NDEA)	0.00790		63	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.0118	63	50 - 150	
N-nitrosopiperidine (NPIP)	0.00400				
N-nitrosomorpholine (NMOR)	ND	0.0365			
N-nitrosopyrrolidine (NPYR)	ND	0.00555			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-16**

Sample Identification: **Rich Liquor 30-40% MEA in water**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 16 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.0104		67	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00460			
N-nitrosodiethylamine (NDEA)	0.00620		67	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.0103	66	50 - 150	
N-nitrosopiperidine (NPIP)	0.00350				
N-nitrosomorpholine (NMOR)	ND	0.0405			
N-nitrosopyrrolidine (NPYR)	ND	0.00685			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-17**

Sample Identification: **Lean Liquor 30-40% MEA in water**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 16 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.00885		63	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00375			
N-nitrosodiethylamine (NDEA)	0.00570		65	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00870	65	50 - 150	
N-nitrosopiperidine (NPIP)	0.00270				
N-nitrosomorpholine (NMOR)	ND	0.0369			
N-nitrosopyrrolidine (NPYR)	ND	0.00535			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-18**

Sample Identification: **451 30-40% MEA in water**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 16 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.0103		70	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00335			
N-nitrosodiethylamine (NDEA)	0.00565		77	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00730	81	50 - 150	
N-nitrosopiperidine (NPIP)	0.00270				
N-nitrosomorpholine (NMOR)	ND	0.0540			
N-nitrosopyrrolidine (NPYR)	ND	0.00425			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-19**

Sample Identification: **510 30-40% MEA in water**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 16 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.0141		77	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00515			
N-nitrosodiethylamine (NDEA)	0.00525		79	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00880	83	50 - 150	
N-nitrosopiperidine (NPIP)	0.00305				
N-nitrosomorpholine (NMOR)	ND	0.0357			
N-nitrosopyrrolidine (NPYR)	ND	0.00435			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

⚐: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-20**

Sample Identification: **512 30-40% MEA in water**

Date Received: 22 February 2011 Date Analysed: 16 March 2011

Date Extracted: 16 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.00920		70	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00390			
N-nitrosodiethylamine (NDEA)	0.00530		71	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00905	73	50 - 150	
N-nitrosopiperidine (NPIP)	0.00340				
N-nitrosomorpholine (NMOR)	ND	0.0367			
N-nitrosopyrrolidine (NPYR)	ND	0.00425			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **89565-BLC**

Sample Identification: **Laboratory Blank C (Applies to sample 89565-14 to -20)**

Date Received: Not Applicable

Date Analysed: 16 March 2011

Date Extracted: 16 March 2011

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.0117		63	50 - 150	
N-nitrosomethylethylamine (NMEA)	ND	0.00485			
N-nitrosodiethylamine (NDEA)	0.00725		65	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.0111	68	50 - 150	
N-nitrosopiperidine (NPIP)	0.00420				
N-nitrosomorpholine (NMOR)	ND	0.0383			
N-nitrosopyrrolidine (NPYR)	ND	0.00500			

Footnotes:

[1] Results are calculated using the average weight of samples in this batch

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: JKM Authorised: P C Bridgen

AsureQuality

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Certificate of Analysis

Date Issued: 30 November 2010

Client: CSIRO Energy Technology
West Entrance, Riverside Corporate Park, Delhi Rd
West Ryde
NSW, 2113
Australia

Attention: Phil Jackson

AsureQuality Lab. Reference: 84132

Sample Type(s): Aqueous

Analysis: **Nitrosamines**

Method: In-House HRGC-HRMS Method (Isotope Dilution)

Results are reported in milligrams per litre (mg/L), equivalent to ppm, on an as received basis to three significant figures. The DL value is reported to three significant figures. Results have been corrected for recoveries.

Unless requested otherwise, samples will be disposed of three months from the date of this report.

Comments:
None.

Phil Bridgen
Scientist
AsureQuality Limited

ilac-MRA 131 new zealand accredited laboratory

Results: Nitrosamines

Laboratory Reference: **84132-1**

Sample Identification: **Sample 1, 30 wt% MEA 0.98mol NaHCO3**

Date Received: 16 November 2010 Date Analysed: 29 November 2010

Date Extracted: 29 November 2010

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.510		35	50 - 150	⚐
N-nitrosomethylethylamine (NMEA)	ND	0.0208			
N-nitrosodiethylamine (NDEA)	0.0612		50	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.113	53	50 - 150	
N-nitrosopiperidine (NPIP)	ND	0.0428			
N-nitrosomorpholine (NMOR)	19.0				
N-nitrosopyrrolidine (NPYR)	ND	0.0436			
N-nitrosodi-n-butylamine (NDBA)[5]	ND	0.213			

Footnotes:

[1] Results are reported on an as received basis
[2] Sample specific estimated detection limit
[3] Labelled internal standard (IS) recovery
[4] Lower control limit - upper control limit for IS recovery
[5] Results for this analyte is not accredited

Abbreviations:

ND: Not detected
⚐: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: PB Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **84132-BLA**

Sample Identification: **Laboratory Blank A (applies to sample 84132-1)**

Date Received: Not Applicable

Date Analysed: 29 November 2010

Date Extracted: 29 November 2010

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.519		39	50 - 150	R
N-nitrosomethylethylamine (NMEA)	ND	0.024			
N-nitrosodiethylamine (NDEA)	0.064		54	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.115	58	50 - 150	
N-nitrosopiperidine (NPIP)	ND	0.0372			
N-nitrosomorpholine (NMOR)	0.196				
N-nitrosopyrrolidine (NPYR)	ND	0.0480			
N-nitrosodi-n-butylamine (NDBA)[5]	ND	0.476			

Footnotes:

[1] Results are calculated using the average weight of samples in this batch

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

[5] Results for this analyte is not accredited

Abbreviations:

ND: Not detected

R: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: PB Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **84132-2**

Sample Identification: **Sample 2, 30 wt% MEA 0.98mol NaHCO3**

Date Received: 16 November 2010 Date Analysed: 29 November 2010

Date Extracted: 29 November 2010

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.658		39	50 - 150	⚑
N-nitrosomethylethylamine (NMEA)	0.698				
N-nitrosodiethylamine (NDEA)	0.723		53	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	0.763		57	50 - 150	
N-nitrosopiperidine (NPIP)	0.709				
N-nitrosomorpholine (NMOR)	ND	0.00918			
N-nitrosopyrrolidine (NPYR)	0.755				
N-nitrosodi-n-butylamine (NDBA)[5]	0.718				

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

[5] Results for this analyte is not accredited

Abbreviations:

ND: Not detected

⚑: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: PB Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **84132-3**

Sample Identification: **Sample 3, 30% w/w MEA 1M KHCO3 (3 Bottles)**

Date Received: 16 November 2010 Date Analysed: 29 November 2010

Date Extracted: 29 November 2010

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.0312		40	50 - 150	Ꝑ
N-nitrosomethylethylamine (NMEA)	ND	0.00183			
N-nitrosodiethylamine (NDEA)	0.00353		53	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00845	58	50 - 150	
N-nitrosopiperidine (NPIP)	ND	0.00380			
N-nitrosomorpholine (NMOR)	ND	0.0103			
N-nitrosopyrrolidine (NPYR)	ND	0.00355			
N-nitrosodi-n-butylamine (NDBA)[5]	ND	0.0187			

Footnotes:

[1] Results are reported on an as received basis

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

[5] Results for this analyte is not accredited

Abbreviations:

ND: Not detected

Ꝑ: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: PB Authorised: P C Bridgen

Results: Nitrosamines

Laboratory Reference: **84132-BLB**

Sample Identification: **Laboratory Blank B (applies to sample 84132-2 and 3)**

Date Received: Not Applicable

Date Analysed: 29 November 2010

Date Extracted: 29 November 2010

Analyte	Conc.[1] (mg/L)	DL[2]	IS %REC[3]	LCL-UCL[4]	Qualifiers
N-nitrosodimethylamine (NDMA)	0.0324		39	50 - 150	Þ
N-nitrosomethylethylamine (NMEA)	ND	0.00150			
N-nitrosodiethylamine (NDEA)	0.00400		54	50 - 150	
N-nitrosodi-n-propylamine (NDPA)	ND	0.00718	58	50 - 150	
N-nitrosopiperidine (NPIP)	ND	0.00233			
N-nitrosomorpholine (NMOR)	0.0123				
N-nitrosopyrrolidine (NPYR)	ND	0.00300			
N-nitrosodi-n-butylamine (NDBA)[5]	ND	0.0298			

Footnotes:

[1] Results are calculated using the average weight of samples in this batch

[2] Sample specific estimated detection limit

[3] Labelled internal standard (IS) recovery

[4] Lower control limit - upper control limit for IS recovery

[5] Results for this analyte is not accredited

Abbreviations:

ND: Not detected

Þ: IS recovery outside method guidelines

Lab Analyst: NE Data Analyst: PB Authorised: P C Bridgen