



Report No. 573

Waters Proficiency Testing

Sub-Program 99

-Nitrosamines-

May 2008

Acknowledgments

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1. Foreword

This report summarises the results of a proficiency testing program on the determination of N-Nitrosodimethylamine, N-Nitrosodi-n-propylamine and N-Nitrosodiphenylamine in water. This is sub-program 99 in a planned series of programs involving the analysis of chemical and physical parameters of waters.

The exercise was conducted in March 2008 by Proficiency Testing Australia (PTA). The main aim of the program was to assess laboratories' abilities to competently perform the prescribed analyses.

The Technical Advisor for the program was Mr M Wright from MGT Environmental Consulting Pty Ltd and the Program Coordinator was Ms L Russell from PTA.

2. Program Features and Design

- 2.1 Each laboratory was randomly allocated a unique code number for the program to ensure confidentiality of results. Reference to each laboratory in this report is by code number only.
- 2.2 Laboratories were provided with the "Instructions to Participants" and "Results Sheet" (see Appendix C).
- 2.3 Participants were provided with one glass ampoule labelled A7008 containing nitrosamines.
- 2.4 A total of 13 laboratories received samples, comprising:
 - 12 Australian participants; and
 - 1 overseas participant.

Of these 13 laboratories, 2 were unable to submit results by the due date.

- 2.5 Results (as reported by participants) with corresponding summary statistics (i.e. number of results, median, normalised interquartile range, minimum, maximum and range) are presented in Appendix A (for each sample and for each of the analyses performed).
- 2.6 A robust statistical approach, using z-scores, was utilised to assess laboratories' testing performance (see Section 3). Robust z-scores, and z-score charts relevant to each test are presented in Appendix A.

The document entitled *Guide to Proficiency Testing Australia, 2008* (reference [1]) defines the statistical terms and details the statistical procedures referred to in this report.

- 2.7 A tabulated listing of laboratories (by code number) identified as having extreme or outlier results can be found on page 6.
- 2.8 All ampoules were subjected to homogeneity and stability testing by the New York State Department of Health, Wadsworth Center for Laboratories & Research. On the basis of this testing, the ampoules utilised for this program were considered to be homogeneous and any results identified as extreme could not be attributed to ampoule variability.
- 2.9 The ampoules were considered to be stable for the testing period (one month) plus a further eleven months if unopened and refrigerated (2°C – 5°C).

3. Statistical Format

For each test, where appropriate, the following information is given:

- a table of results and calculated z-scores;
- a list of summary statistics; and
- ordered z-score charts.

3.1 Outlier Results and Z-scores

In order to assess laboratories' testing performance, a robust statistical approach, using z-scores, was utilised. Z-scores give a measure of how far a result is from the consensus value (i.e. the median), and gives a "score" to each result relative to the other results in the group.

A z-score close to zero indicates that the result agrees well with those from other laboratories. Whereas, a z-score with an absolute value greater than three is considered to be an outlier and is marked by the symbol "S".

Each determination was examined for outliers with all methods pooled. The table on page 6 summarises the outlier results detected.

3.2 Results Tables and Summary Statistics

Each of these tables contains the results returned by each laboratory, including the code number for the method used, and the robust z-score calculated for each result.

Results have been entered exactly as reported by participants. That is, laboratories which did not report results to the precision (i.e. number of significant figures) requested on the Results Sheet have **not** been rounded to the requested precision before being included in the statistical analysis.

A list of summary statistics appears at the bottom of each of the tables of results and consists of:

- the number of results for that test/sample (*No. of Results*);
- the median of these results, i.e. the middle value (*Median*);
- the normalised interquartile range of the results (*Normalised IQR*);
- the robust coefficient of variation, expressed as a percentage (*Robust CV*) - i.e. $100 \times \text{Normalised IQR} / \text{Median}$;
- the minimum and maximum laboratory results; and
- the range (*Maximum - Minimum*).

The median is a measure of the centre of the data.

The normalised IQR is a measure of the spread of the results. It is calculated by multiplying the interquartile range (IQR) by 0.7413, a factor which converts the IQR to an estimate of the standard deviation. The IQR is the difference between the upper and lower quartiles (i.e. the values above and below which a quarter of the results lie, respectively).

Please see reference [1] for further details on these robust summary statistics.

3.3 Ordered Z-Score Charts

On these charts each laboratory's robust z-score is shown, in order of magnitude, and is marked with its code number. From these charts, each laboratory can readily compare its performance relative to the other laboratories.

These charts contain solid lines at +3 and -3, so that outliers are clearly identifiable as those laboratories whose "bar" extends beyond these "cut-off" lines. The y-axis of these charts has been limited, so very large z-scores appear to extend beyond the chart boundary.

4. PTA and Technical Adviser's Comments

- 4.1 The New York State Department of Health, Wadsworth Center for Laboratories and Research have provided acceptance limits:

Analyte	Acceptance Limit (µg/L)
N-Nitrosodimethylamine	13.6-160
N-Nitrosodi-n-propylamine	25.5-114
N-Nitrosodiphenylamine	27.7-159

- 4.2 Except for one result (N-Nitrosodiphenylamine) all participants have reported within these ranges. Overall the performance for this round has been good, as it is noted that N-Nitrosodimethylamine can be difficult to separate from the solvent under certain chromatographic conditions, and N-Nitrosodiphenylamine has a tendency to decompose in the gas chromatographic inlet.

5. Outlier or Extreme Results

Laboratories reporting outlier **or extreme** results are listed in the following table:

Code	Analysis		
	N-Nitrosodimethylamine	N-Nitrosodi-n-propylamine	N-Nitrosodiphenylamine
162			§

¹ A "§" indicates the occurrence of a z-score outlier result (i.e. those results for which $|z\text{-score}| > 3$).

6. References

- [1] *Guide to Proficiency Testing Australia*, 2008 (This document can be found on the PTA website, www.pta.asn.au)

APPENDIX A

Results & Data Analysis

N-Nitrosodimethylamine.....	A1
N-Nitrosodi-n- propylamine.....	A3
N-Nitrosodiphenylamine	A6

A1

N-Nitrosodimethylamine Results

N-Nitrosodimethylamine

Results by Laboratory Code

Ampoule A7008				
Lab Code	Result \pm MU ¹ ($\mu\text{g/L}$)		Method Code ²	
162	128	#	3	
173	117	\pm 50	2	
177	135	\pm 27	2	
202	78	\pm 16	2	
335	135	\pm 5.61	3	

No of Results: 5

- ¹ Where reported, results are shown with their corresponding measurement uncertainty (MU).
- ² Please refer to Appendix C (page C3) for method code descriptions.
- ³ A "#" indicates that no result was returned for this sample/test.
- ⁴ There were not enough results reported for this analyte to conduct an accurate statistical analysis.

N-Nitrosodi-n-propylamine Results

N-Nitrosodi-n-propylamine

Results by Laboratory Code

Ampoule A7008					
Lab Code	Result ± MU ¹ (µg/L)	Robust z-score ²	Method Code ³		
114	79 ± 26	-0.48	2		
115	80.2 ± 26.7	-0.33	2		
162	83.0 #	0.00	3		
173	103 ± 41	2.39	2		
177	92 ± 18	1.07	2		
189	65.4 ± 22	-2.10	2		
191	63.0 ± 30.2	-2.39	2		
202	71 ± 14	-1.43	2		
225	88 #	0.60	2		
309	84 #	0.12	2		
335	84.6 ± 3.48	0.19	3		

<i>No of Results:</i>	11
<i>Median:</i>	83.0
<i>Normalised IQR:</i>	8.4
<i>Robust CV:</i>	10.1%
<i>Minimum:</i>	63
<i>Maximum:</i>	103
<i>Range:</i>	40

¹ Where reported, results are shown with their corresponding measurement uncertainty (MU).

² "\$"s denote outliers (i.e. those results for which $|z\text{-score}| > 3$). Robust z-scores are calculated as: $z = (A - \text{median}) \div \text{normalised IQR}$, where, A is the participant laboratory's result.

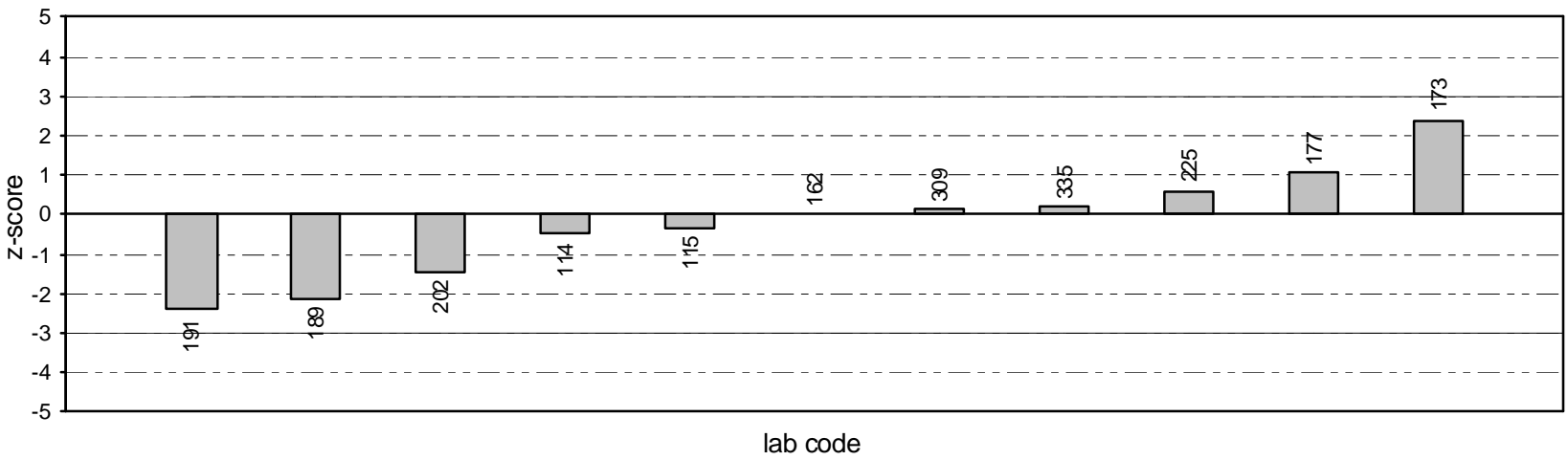
³ Please refer to Appendix C (page C3) for method code descriptions.

⁴ A "#" indicates that no result was returned for this sample/test.

**N-Nitrosodi-n-propylamine -
Ampoule A7008**

Ordered Robust Z-Score Charts

N-Nitrosodi-n-propylamine- Ampoule A7008 - Robust Z-Scores



N-Nitrosodiphenylamine Results

N-Nitrosodiphenylamine***Results by Laboratory Code***

Ampoule A7008				
Lab Code	Result ± MU ¹ (µg/L)	Robust z-score ²	Method Code ³	
114	64 ± 18	-0.42	2	
115	78.0 ± 21.4	0.03	2	
162	188 #	3.62 §	3	
173	118 ± 47	1.34	2	
177	82 ± 16	0.16	2	
189	66.6 #	-0.34	2	
202	56 ± 11	-0.69	2	
225	76 #	-0.03	2	
309	40 #	-1.21	2	
335	114 ± 15.3	1.21	3	

<i>No of Results:</i>	10
<i>Median:</i>	77.0
<i>Normalised IQR:</i>	30.7
<i>Robust CV:</i>	39.8%
<i>Minimum:</i>	40
<i>Maximum:</i>	188
<i>Range:</i>	148

¹ Where reported, results are shown with their corresponding measurement uncertainty (MU).

² "§"s denote outliers (i.e. those results for which $|z\text{-score}| > 3$). Robust z-scores are calculated as: $z = (A - \text{median}) \div \text{normalised IQR}$, where, A is the participant laboratory's result.

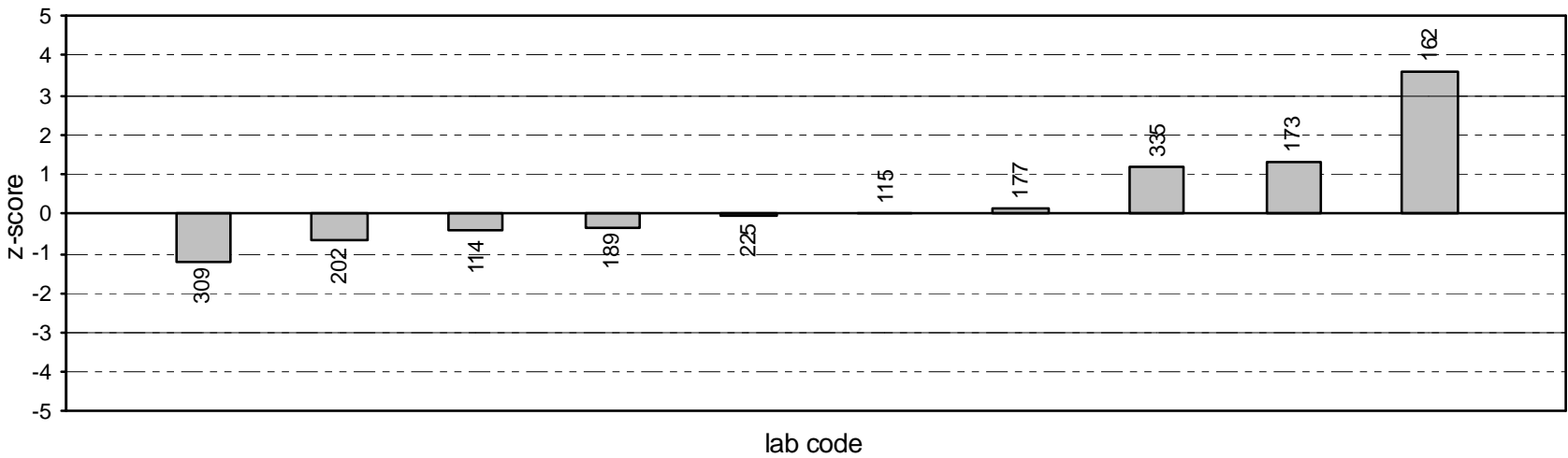
³ Please refer to Appendix C (page C3) for method code descriptions.

⁴ A "#" indicates that no result was returned for this sample/test.

**N-Nitrosodiphenylamine -
Ampoule A7008**

Ordered Robust Z-Score Charts

N-Nitrosodiphenylamine- Ampoule A7008 - Robust Z-Scores



APPENDIX B

Sample Homogeneity

Homogeneity Testing.....	B1
Stability.....	B1

Homogeneity Testing

Samples for this program were obtained from the New York State Department of Health, Wadsworth Center for Laboratories and Research. This organisation is a NIST accredited provider. As such, all samples are subjected to rigorous stability and homogeneity testing. On the bases of this testing, the ampoules utilised for this program were considered to be homogeneous.

Stability

Unopened ampoules are stable for a minimum of twelve (12) months if stored at 2°C – 5°C.

APPENDIX C

Documentation

Instructions to Participants.....	C1
Method Codes.....	C3
Results Sheet.....	C4

**WATERS PROFICIENCY TESTING PROGRAM****CHEMICAL ANALYSIS SUB-PROGRAM 99**

March 2008

NITROSAMINES**INSTRUCTIONS TO PARTICIPANTS**

Please note the following before commencing the analysis of the samples.

1. Samples

- i) One sealed glass ampoule labelled A7008, supplied by the New York State Department of Health, Wadsworth Center for Laboratories and Research. The ampoule contains nitrosamines.
- ii) The ampoule will require 1000 -fold dilution in reagent grade water.

2. Sample Preparation

Caution: Analysis must begin immediately after ampoule is opened.

- i) Adjust ampoule temperature to 20° C.
- ii) Add approximately 900 millilitres (900 mL) of reagent grade water to a one- litre (1L) volumetric flask.
- iii) Record the ampoule ID number. Open the ampoule by snapping the top off at the narrow area of the neck.
- iv) Using a 1.00 millilitre (mL) glass syringe transfer 1.00 millilitre (mL) from the ampoule into the flask.
- v) bring to volume with reagent grade water.
- vi) Stopper and mix by inversion.

3. Tests Requested

For the sample prepared from the ampoule.

- i) N- Nitrosodimethylamine**
- ii) N- Nitrosodi-n-propylamine**
- iii) N-Nitrosodiphenylamine**

(Analyse a reagent water blank by the same method used to analyse samples.)

Participants are requested to perform all tests for which NATA accreditation is held, using their accredited method. Participants are welcome to report results for any of these tests even if NATA accreditation is not held.

If unable to perform the above please note this on your Results Sheet.

4. Safety

- i) Samples are for laboratory use only.
- ii) Participants should have sufficient experience and training to take the necessary precautions when handling the ampoules, prepared samples, other chemicals required for the analysis, and materials for disposal.
- iii) Use of safety glasses, gloves, and fume hoods, where appropriate during the determinations, is recommended.

5. Reporting

- (a) Report results using three significant figures. For compounds not found, report results using < preceding the laboratory's reporting limit.
 - (b) Report results in micrograms per litre ($\mu\text{g/L}$).
 - (c) Do not correct results for recovery.
 - (d) In addition to reporting the results, record the method of analysis using the attached codes.
 - (e) Laboratories are also requested to calculate and report an estimate of uncertainty measurement for each reported measurement result. All estimates of uncertainty of measurement must be given as a 95% confidence interval (coverage factor $k \approx 2$) and reported in $\mu\text{g/L}$.
6. Testing should commence as soon as possible after receiving ampoules and results reported **NO LATER THAN 31 MARCH 2008 to:**

Ms Lexie Russell Proficiency Testing Australia P O Box 1122 ARCHERFIELD BC QLD 4108 AUSTRALIA Phone: +61 7 3721 7373 Fax: +61 7 3217 1844 Email: lrussell@pta.asn.au
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7. For this program your laboratory has been allocated the code number shown on the attached Results Sheet. All reference to your laboratory in reports associated with the program will be through this code number, thus ensuring the confidentiality of your results.

Method Codes to be used for the Results Sheet

ANALYSIS	METHOD DESCRIPTION	METHOD REFERENCE	CODE	
N-Nitrosodimethylamine N-Nitrosodi-n-propylamine N- Nitrosodiphenylamine	GC/MS	SM 19, SM 20, SM 21 (Part 6410B)	1	
		US EPA 8270C	2	
		Other (please specify)	3	
			US EPA 1625	4
			US EPA 607	5
			US EPA 625	6
			Other (please specify)	7

Method Reference Key

(a) SM19, SM20, SM21

APHA "Standard Methods for the Examination of Water and Wastewater" 19th Edition (1995), 20th Edition (1998), 21st Edition (2005)

(b) USEPA

USEPA SW – 846.



PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS SUB-PROGRAM 99

NITROSAMINES MARCH 2008

RESULTS SHEET

($\mu\text{g/L}$)

Laboratory
Code

ANALYSIS	AMPOULE A7008		Method Code
	Result	$\pm\text{MU}^*$	
N-Nitrosodimethylamine			
N-Nitrosodi-n-propylamine			
N-Nitrosodiphenylamine			

- (a) For each prepared sample (diluted from the ampoule) only a single result is requested.
- (b) Report results using three significant figures. For compounds not found, report results using < preceding the laboratory's reporting limit.
- (b) Report results in micrograms per litre ($\mu\text{g/L}$)
- (c) Do not correct results for recovery
- (d) MU^* Laboratories Measurement Uncertainty (MU) if known for the result. Please report in $\mu\text{g/L}$

DATE

SIGNATURE

<p>Return results NO LATER THAN 31 MARCH 2008 to: Ms Lexie Russell, Proficiency Testing Australia P O Box 1122 ARCHERFIELD BC QLD 4108 AUSTRALIA</p>	<p>Phone: +617 3721 7373 Fax: +617 3217 1844 Email: lrussell@pta.asn.au</p>
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End of Report