Intercomparison Of Density Facilities

A Report for

NMSPU,
Department of Trade and Industry
151 Buckingham Palace Road
London, SW1W 9SS

Project No: DSDC40

Report No: 057/2000

Date: 24 March 2000

This report is issued as part of the contract under which the work has been carried out for the client.

NOTES

1 This report may be published in full by the client unless it includes information supplied in confidence by NEL or any third party. Such information, if included within the report, shall be separately designated as confidential by NEL.

2a The prior written consent of NEL shall be obtained by the client before publication by him or any extract from, or abridgement of, this report.

2b The prior written consent of NEL shall be obtained by the client before publication:

- where such publication is made in connection with any public enquiry, legal proceedings or arbitration
- where such publication is made in, or in connection with, any company prospectus or similar document
- where the client has notice that NEL is seeking or intends to seek patent or like protection for any intellectual property produced in the course of rendering the services.

Flow Centre

National Engineering Laboratory
East Kilbride
Glasgow G75 0Qu
Tel: 01355 220222
Fax: 01355 272999

INTERCOMPARISON OF DENSITY FACILITIES

A Report for

NMSPU
Department of Trade and Industry
151 Buckingham Palace Road
London, SW1W 9SS

SUMMARY

This work was undertaken as part of the 1996-1999 Flow Programme on behalf of the NMSPU. The project activities were aimed at maintaining and developing measurement standards for density and of supporting the framework by which traceability and calibrations are made available to industry throughout the UK.

It is not yet possible to draw rigorous conclusions until results are available from NIST(Boulder) and PTB. The NEL data set has excellent repeatability and consistency and agrees with the limited, but precise, measurements produced by NIST(Gaithersburg) to well within the combined uncertainties. The NRLM measurements differ systematically from the trend of both the NIST(Gaithersburg) and NEL data.

The results of this intercomparison will be of immediate benefit to industry since, apart from water substance, there are no normal liquids for which accurate and traceable density data exist at greater than atmospheric pressure. The current restrictions on calibration at elevated pressure will be alleviated and industry's capability to calibrate industrial densitometers accurately and traceably at actual metering conditions much enhanced.

Prepared by: Mr J T R Watson ....

Approved by: Dr B Millington ....

Date: 24 March 2000
for Dr F C Kinghorn
Director

CONTENTS

1 INTRODUCTION

This project was undertaken by the National Engineering Laboratory as part of the 1996-1999 Flow Programme on behalf of the National Measurement System Policy Unit. The principal objective of this proposal was to support the UK's industrial capability for the calibration of flow meters, on which fluid density has a direct and important influence. The project activities are aimed at maintaining and developing measurement standards for density and of supporting the framework by which traceability and calibrations are made available to industry throughout the UK.

NEL is an industrial research establishment, a business of TÜV Product Service Ltd, concerned with many areas of engineering research. The Flow Centre at NEL is the custodian of the UK National Standards for flow measurement including primary standards for the density of gases and liquids at elevated pressure. Facilities exist for calibration and research involving gas, water, oil, and multiphase flow measurement devices. All the facilities are fully traceable to the base primary standards of measurement and most are NAMAS accredited.

On commencement of this project a project outline was prepared and submitted to national delegates at the 1998 annual meeting of EUROMET, calling for EC laboratories to participate in an intercomparison of density facilities. Though the project proposal received significant support and many immediate expressions of interest it transpired that there were no national laboratories other than PTB and NEL capable of undertaking traceable measurements of liquid density at the required conditions. As a consequence the call was opened to international laboratories. The agreed participants in the intercomparison are:

NIST, Boulder, USA;	NIST, Gaithersburg, USA;
NRLM, Japan;	PTB, Germany; and
NEL, UK.	

It should be noted that the results of this intercomparison will be of immediate benefit to industry. Apart from water substance, there are no normal liquids for which accurate and traceable density data exist at pressures greater than atmospheric. The availability of an additional transfer standard, a liquid of known and traceable density, will enable calibration laboratories, densitometer manufacturers and users of densitometers in the process industries to undertake more accurate, reliable and traceable calibrations of these devices. The current restrictions on calibration at elevated pressure will be reduced and the capability to calibrate industrial densitometers accurately and traceably at actual metering conditions enhanced.

2 PROJECT OBJECTIVES

The project objectives were to undertake an intercomparison of measurement standards for the density of liquids at elevated pressure.

Each participant agreed to undertake a series of measurements over all, or as wide an extent as was practicable, of a defined range of conditions on a suitable transfer standard liquid. An intercomparison of the findings would be made which would enable the participating organisations to validate further the operation of their measurement facilities. The defined range of measurement conditions was:

$$0 \le t/^{o}C \le 80; \quad \text{and} \quad 0.1 \le p/MPa \le 30.$$

Since the capabilities of each laboratory differ, however, individual measurement programmes were established, which either covered or overlapped the defined range of conditions. The individual measurement ranges were:-

Participant	Temperature Range	Pressure Range	Status
NIST(Gaithersburg)	15 to 25°C	ambient pressure	Completed
NIST(Boulder)	0 to 100°C	0.1 to 30 MPa	Not yet begun
NRLM	25 to 100°C	0.1 to 30 MPa	Completed
PTB	15 to 85°C	0.1 to 35 MPa	In progress
NEL	0 to 80°C	0.1 to 30 MPa	Completed

3 SELECTION OF TRANSFER STANDARD

The transfer standard liquid was selected to be chemically stable over the lifetime of the tests, non-corrosive, non-hydroscopic, and capable of being degassed without change of composition. The liquid selected for this purpose was high-purity toluene (methylbenzene; $C_6H_5CH_3$).

Purified toluene samples were prepared at considerable risk and expense by Dr Tom Bruno (NIST, Division 838, Boulder, Colorado) and shipped in 500 ml quantities to each participant. To prevent contamination and degradation of the samples they were supplied in electropolished stainless steel (304L) vessels under an atmosphere of helium. The purified toluene was carefully mixed prior to distribution to ensure uniform composition. Analysis indicated a sample purity of 99.92%.

4 MEASUREMENTS

Silicon is a primary reference material whose density is defined at near ambient temperatures and pressures. National primary standard facilities for the determination of the density of liquids therefore utilise silicon artifacts in their hydrostatic weighing system. However, such national facilities are only capable of operation over a narrow range of conditions and are not suitable for use at elevated pressure. The densitometer operated by the Fluid Flow Group at NIST (Gaithersburg) is based on the use of a silicon artifact. The NEL densitometer is national standard for the density of liquids at elevated pressure. It also operates on the hydrostatic weighing principle but the density of its fused silicon artifact is determined from the known density of pure water at ambient temperature and pressure. None of the other densitometers involved in the study are national standard facilities. The NIST (Boulder), the PTB, and the NRLM densitometers also operate on the hydrostatic weighing principle and, like the NEL densitometer, are dependent on the known density of water for the calibration of their artifacts.

<u>The understanding reached by the participants in this intercomparison is that, in general, we are comparing measurements of liquid density at elevated pressures produced by state-of-the-art experimental facilities. The magnetic densitometer at NRLM is a new apparatus that is still in its development stage.</u>

Of the five participants only three, NIST(Gaithersburg), NLRM and NEL, have as yet completed their experimental programmes. Results are still awaited from NIST(Boulder) and PTB. Both of the latter have experienced delays due to the breakdown or malfunction of key elements of their measurement facilities. It is expected that both these sets of measurements will be available by the end of May 2000.

4.1 NIST (Gaithersburg)

The measurements at NIST were undertaken by Drs Vern E. Bean and John F. Houser. The purified toluene samples for the density intercomparison were provided by NIST (Boulder). Cylinders, numbered 8 and 9, and containing 384.7 g and 387 g, respectively, were received by the Fluid Flow Group of Division 836 at NIST, Gaithersburg, Maryland.

4.1.1 Measurement Programme

The density was measured at a nominal 15°C, 20°C, and 25°C and at atmospheric pressure in a primary standard, hydrostatic weighing apparatus.

4.1.2 Methodology

The hydrostatic weighing apparatus is comprised of a sensitive electronic balance mounted above the sample container, which is inside a controlled temperature bath. The weighing artefact is a single crystal of silicon of known density, which is supported by a special weight hanger suspended by a filament of polyamide from the bottom hook of the balance. The small diameter (0.15 mm) of the filament and material from which the filament is made were selected to mitigate surface tension effects between the fluid and the filament. The silicon crystal is off-loaded from the weight hanger by raising the temperature bath and the sample cell as a unit such that the crystal rests on a post on the bottom of the sample container and the hanger hangs free. The raising and lowering of the temperature bath and sample container changes the length of filament that is under the fluid surface and hence changes the fluid buoyancy force on the filament. Appropriate corrections are applied to the data for this effect.

The double substitution weighing design was used. The uncertainty for the weighing process is 1.8 ppm, which is equivalent to 0.00156 kg/m^3 at 20°C, with a coverage factor of 1.

4.1.3 Data Analysis

The density measurements were made on the following dates:

Date	Temperature/°C
24 August 1999	15
25 August 1999	20
26 August 1999	25
27 August 1999	15
28 August 1999	20
30 August 1999	25

Seven density determinations were made each day. The data is best described by the expression:

$$\rho = 885.329367 - 0.918491 \cdot t - 0.0003100 \cdot t^2 \, , \qquad (1)$$

where ρ is the density of the toluene in kg/m^3; and
t is the temperature in °C.

The standard error of the fit is 0.00432 kg/m^3. The density of the toluene at 20°C is 866.8355 ± 0.0092 kg/m^3 where the expanded uncertainty is $2 \cdot \left[(0.00156)^2 + (0.00432)^2 \right]^{\frac{1}{2}}$.

4.2 NRLM

The measurements at NRLM were undertaken by Dr Ryohei Masui. Dr Masui's detailed report on his measurements on toluene is reproduced in the Appendix. It should be noted that the magnetic densitometer at NRLM is a new facility and still in a development phase. The 66 measurements of toluene density are reported to have an uncertainty at a 95% confidence level of around 0.05%.

4.3 NEL

Cylinders, numbered 3 and 4, and containing 331.3 and 325.7 g of toluene, respectively, were received by the Flow Centre at NEL. Both samples had a reported purity of 99.92%. The content of cylinder No 3 was used in this work.

4.3.1 Measurement Programme

Density measurements were made on nine isotherms from 0°C to 80°C at intervals of 10°C. On each isotherm measurements were made at six pressures in the interval 0.1 to 30 MPa. The increments of pressure were selected to give near uniform changes in density. The programme made provision for repeat measurements at several pressures on each isotherm.

During the final sequence of measurements the sinker became detached from its suspension and the pressure vessel had to be dismantled and the test sample discarded. As a consequence of this equipment failure there are no measurements of density at ambient pressure and 80°C. All 95 measurements of density obtained with test fluid from sample cylinder No 3 are reported in Table 1.

4.3.2 Methodology

The NEL liquid densitometer is a hydrostatic balance densitometer used in conjunction with a magnetic suspension coupling [1,2]. The method of operation is outlined briefly below but is described in detail in Reference 3. Recently the density range of the facility has been extended following conversion to the new single-sinker form, as described in reference 4, but these changes should have little influence on the measurements reported here.

The NEL liquid densitometer utilises a single sinker: a gold-plated solid cylinder of fused quartz with a volume of some 24 cm^3. A thin stainless steel rod connected to a simple mechanism links the sinker to a microbalance via an electronically controlled magnetic-suspension coupling. The latter transmits the sinker load through the wall of the pressure vessel to the microbalance at ambient conditions. Each measurement of density is obtained from ten readings of the weight of the sinker in the test fluid.

The major uncertainty associated with this method of measurement arises from the determination of the volume of the sinker and its dilation with temperature and pressure. The volume of the latter is established by careful weighing of the quartz sinker and its associated stainless steel suspension in both air and pure water at near ambient conditions.

The temperature of the densitometer is measured by four 25 ohm standard platinum-resistance thermometers attached around the periphery of the pressure vessel. The vessel is immersed in a temperature-controlled bath, which is stable to within 1 mK over its operating range. The total uncertainty in the temperature of the test fluid in the densitometer is assessed as 4 mK at a 95% confidence level.

A differential pressure indicator (DPI) is used to compare the pressure of the test fluid with that of nitrogen from a gas-operated pressure balance. The uncertainty in the measurement of differential pressure is less than 100 Pa. The absolute pressure of the test fluid in the densitometer is obtained from the atmospheric pressure, gas-operated pressure balance and DPI readings, corrected for temperature effects and pressure heads in the connecting lines as necessary. The uncertainty in the calculated total pressure is assessed as less than 0.01% at a 95% confidence level.

The total uncertainty in the reported measurements of density is obtained from the expression:

$$U_\rho = \left[U^2_{\rho,method} + \left(\frac{\partial \rho}{\partial T}\right)^2_p \cdot U_T^2 + \left(\frac{\partial \rho}{\partial p}\right)^2_T \cdot U_p^2 \right]^{1/2} ,$$

where the partial derivatives are obtained from an equation of state fitted to the measured values of density.

Over the full operational range of the facility the total uncertainty in density is 0.015% at a 95% confidence level. However, over the limited temperature range investigated here the total uncertainty of measurement is within 0.010%.

4.3.3 Data Analysis

To establish the consistency and reproducibility of the data all 95 measurements were regressed to a simple equation of the form:

$$\begin{aligned} \rho / \rho_0 = {} & a_1 + a_2 \cdot \pi + a_3 \cdot \pi^2 + a_4 \cdot \pi^3 + \theta.(a_5 + a_6 \cdot \pi + a_7 \cdot \pi^2 + a_8 \cdot \pi^3) + \\ & \theta^2.(a_9 + a_{10} \cdot \pi + a_{11} \cdot \pi^2) + \theta^3.(a_{12} + a_{13} \cdot \pi) \end{aligned} \tag{2}$$

where
- ρ is the density in kg/m^3;
- θ is a reduced temperature, $\theta = t / t_0$;
- t is the temperature in Celsius on the ITS-90 scale;
- π is a reduced pressure, $\pi = p / p_0$;
- p is the absolute pressure in MPa;
- $\rho_0 = 1000$ kg/m^3, $t_0 = 100$ °C and $p_0 = 30$ MPa.

Eqn (2) represents the NEL data set to within minimum and maximum deviations of –8 and +10 parts per million (ppm) respectively. All coefficients in the equation were fully significant at a 95% confidence level: the values of the coefficients obtained from the regression analysis were:

a_1	$8.85245817 \times 10^{-1}$	a_8	$1.04758773 \times 10^{-3}$
a_2	$2.03991231 \times 10^{-2}$	a_9	$-7.22876573 \times 10^{-4}$
a_3	$-2.13930160 \times 10^{-3}$	a_{10}	$5.25149475 \times 10^{-3}$
a_4	$2.39760689 \times 10^{-4}$	a_{11}	$-2.18842943 \times 10^{-3}$
a_5	$-9.22995334 \times 10^{-2}$	a_{12}	$-2.40906978 \times 10^{-3}$
a_6	$1.19801477 \times 10^{-2}$	a_{13}	$1.09274442 \times 10^{-3}$
a_7	$-3.38580027 \times 10^{-3}$		

The 95 measurements of temperature, pressure and density are reported in Table 1 together with values of density calculated from Eqn (2) and the percentage agreement between the two. The total uncertainty in the measured values of density is assessed as 0.01% at a 95% confidence level. The repeat measurements of density agree to within a few parts per million.

5 INTERCOMPARISON

Density values derived from the NEL equation, Eqn (2), at near ambient temperature and 0.1 MPa are given in the following table and compared with the values of density calculated from the NIST (Gaithersburg) Equation, Eqn (1).

t / °C	**NEL** $\rho_{EQN(2)}$ /(kg/m^3)	**NIST** $\rho_{EQN(1)}$ **/(kg/m^3)**	**% difference**
15	871.451	871.482	-0.0036
20	866.814	866.836	-0.0025
25	862.167	862.173	-0.0007

The NIST (Gaithersburg) and NEL results are consistent to well within the combined uncertainties of both sets of data. It should be noted that the pressure at which the NIST results were obtained is not defined. If the pressure differs from 0.1 MPa then at 20°C a density correction of some 0.077 kg/m^3 per 0.1 MPa needs to be applied.

In Figure 1 the measurements of NRLM and NIST (Gaithersburg) are compared with the mean surface through the NEL measurements. The reproducibility and consistency of the NRLM results are less than for the other two sources. It should be noted that the NRLM facility is still in its development phase.

6 CONCLUSIONS

It is not possible to draw rigorous conclusions until results are available from both NIST (Boulder) and PTB. From the limited data sets available it can be seen that:

- the NEL data have a repeatability of several parts per million;
- the NEL data set appear consistent to within ten parts per million over the temperature and pressure range investigated in this work;
- the NEL and NIST (Gaithersburg) measurements agree to well within their combined uncertainties; and
- the NRLM measurements differ systematically from the trend of both the NIST (Gaithersburg) and NEL data.

REFERENCES

1 LÖSCH, H. W. Entwicklung und Aufbau von neuen Magnetschwebewaagen zurberührungsfreien Messung vertikaler Kräfte. VDI Fortschritt-Berichte, Reihe 3, Nr. 138, Düsseldorf 1987.

2 LÖSCH, H. W., KLEINRAHM, R., and WAGNER, W. Neue Magnetschwebewaagen fürgravimetrische Messungen in der Verfahrenstechnik. VDI-GVC Jahrbuch 1994, Düsseldorf 1994.

3 WATSON, J. T. R., FERGUSON D., and RYAN, G. 'National Standard Facilities For The Density Of Liquids And Gases At Elevated Pressures'. Paper presented at the Density Seminar held in the James Watt Conference Centre, NEL, on 24 October, 1994, in conjunction with the North Sea Flow Measurement Workshop, 1994.

4 WAGNER, W., BRACHTHAUSER, K., KLEINRAHM, R., and LÖSCH, H. W. A New, Accurate Single-Sinker Densitometer for Temperatures from 233 to 523 K at Pressures up to 30 MPa. Int. J. Thermophys., 1995, Vol. 16(2), p 399-411.

LIST OF TABLES

LIST OF FIGURES

Table 1

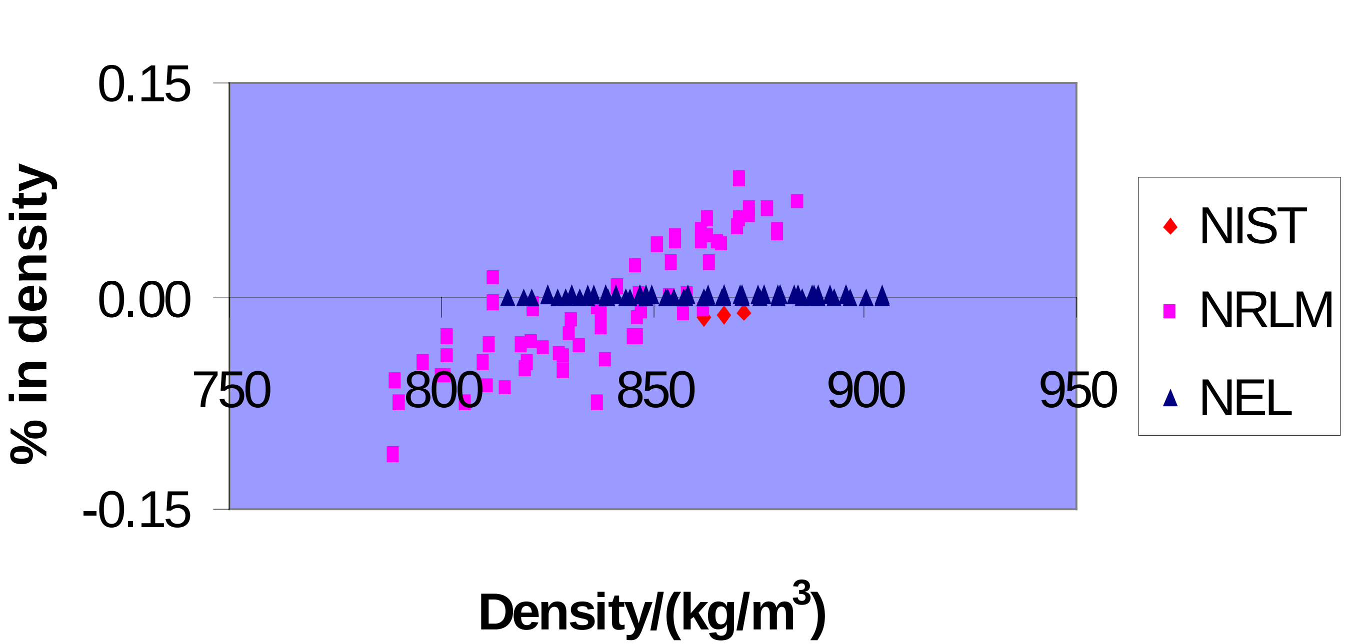
Experimental Results - NEL

t/°C	p/MPa	ρ/(kg/m^3)	$\rho_{EQN(2)}$/(kg/m^3)	% difference
0.009	5.603	888.974	888.975	-0.0001
0.009	11.609	892.823	892.825	-0.0002
0.010	17.615	896.523	896.526	-0.0003
0.010	23.622	900.086	900.090	-0.0005
0.011	30.130	903.809	903.809	0.0000
0.009	30.130	903.810	903.811	-0.0001
0.009	5.604	888.974	888.975	-0.0001
0.010	5.604	888.975	888.974	0.0001
10.009	5.604	879.963	879.958	0.0006
10.012	5.604	879.962	879.955	0.0008
10.009	30.131	895.574	895.572	0.0003
10.009	30.131	895.572	895.572	0.0001
10.009	23.624	891.670	891.666	0.0004
10.011	17.618	887.922	887.919	0.0003
10.010	11.612	884.024	884.023	0.0001
10.010	5.605	879.960	879.957	0.0003
20.010	5.605	870.932	870.930	0.0002
20.010	30.131	887.369	887.370	-0.0001
20.009	23.624	883.275	883.272	0.0004
20.010	17.618	879.336	879.334	0.0002
20.010	11.611	875.227	875.227	0.0000
20.011	5.605	870.931	870.929	0.0002
30.010	5.605	861.879	861.880	-0.0001
30.010	30.131	879.197	879.200	-0.0003
30.010	23.623	874.900	874.898	0.0002
30.011	17.116	870.404	870.404	0.0000
30.009	11.109	866.054	866.057	-0.0003
30.011	5.603	861.877	861.878	-0.0001
40.010	5.603	852.790	852.792	-0.0003
40.011	30.129	871.048	871.051	-0.0004
40.011	23.623	866.540	866.538	0.0002
40.011	23.623	866.540	866.538	0.0002
40.010	17.116	861.807	861.810	-0.0004
40.011	11.110	857.216	857.219	-0.0003
40.011	11.110	857.215	857.219	-0.0005
40.012	5.604	852.791	852.791	0.0000
50.010	5.604	843.657	843.658	-0.0001
50.011	30.130	862.920	862.921	-0.0001
50.012	23.623	858.186	858.183	0.0004
50.013	17.116	853.201	853.202	-0.0001
50.009	11.110	848.350	848.354	-0.0005
50.010	5.604	843.657	843.658	-0.0001
60.010	5.605	834.458	834.460	-0.0003
60.011	30.131	854.796	854.798	-0.0002
60.013	23.624	849.823	849.822	0.0001
60.012	17.117	844.571	844.576	-0.0006
60.012	11.111	839.442	839.444	-0.0002
60.010	5.605	834.461	834.460	0.0001

Table 1 (Cont)

t/°C	p/MPa	$\rho/(\mathrm{kg/m^3})$	$\rho_{EQN(2)}/(\mathrm{kg/m^3})$	% difference
70.011	5.605	825.189	825.186	0.0004
70.012	5.605	825.191	825.185	0.0008
70.011	30.131	846.678	846.674	0.0005
70.011	23.123	841.041	841.035	0.0007
70.010	17.116	835.919	835.916	0.0004
70.009	11.110	830.489	830.483	0.0007
70.011	5.604	825.193	825.185	0.0010
80.011	5.604	815.819	815.822	-0.0004
80.012	30.129	838.536	838.539	-0.0004
80.012	23.121	832.610	832.612	-0.0002
80.010	23.121	832.609	832.613	-0.0005
80.011	17.114	827.205	827.208	-0.0004
80.011	11.108	821.450	821.452	-0.0002
80.011	5.602	815.813	815.820	-0.0008
0.010	30.131	903.811	903.811	0.0000
0.010	30.131	903.810	903.811	-0.0001
0.010	0.099	885.301	885.304	-0.0003
0.011	11.611	892.820	892.825	-0.0005
0.011	0.099	885.301	885.303	-0.0002
10.010	0.099	876.070	876.068	0.0002
10.010	11.611	884.025	884.023	0.0003
10.010	30.131	895.573	895.571	0.0003
10.010	0.099	876.071	876.068	0.0003
20.010	0.099	866.803	866.804	-0.0002
20.011	30.130	887.370	887.368	0.0002
20.010	11.611	875.227	875.227	0.0000
20.010	0.099	866.803	866.804	-0.0002
30.010	0.099	857.497	857.497	0.0000
30.012	11.610	866.426	866.425	0.0001
30.010	30.130	879.197	879.199	-0.0003
30.010	0.099	857.493	857.497	-0.0005
40.010	0.099	848.131	848.133	-0.0002
40.011	30.130	871.049	871.052	-0.0003
40.010	11.110	857.215	857.220	-0.0006
40.011	0.099	848.132	848.132	0.0000
50.012	0.099	838.700	838.695	0.0006
50.013	11.111	848.350	848.351	-0.0001
50.012	30.131	862.921	862.921	0.0000
50.012	0.100	838.699	838.696	0.0004
60.010	0.100	829.172	829.175	-0.0004
60.011	30.132	854.797	854.799	-0.0002
60.011	11.112	839.441	839.446	-0.0005
60.011	0.100	829.173	829.174	-0.0001
70.013	0.101	819.548	819.550	-0.0002
70.014	11.112	830.486	830.481	0.0006
70.011	11.112	830.488	830.483	0.0006
70.012	30.133	846.680	846.675	0.0006

Figure 1 - Comparison of Toluene Density Measurements



A P P E N D I X

NRLM Measurement Report