ENERGIE **NB** POWER
Point Lepreau G.S.

FUNCTION: ANALYTICAL PROCEDURE	SYSTEM: CHEMISTRY LABORATORY	UNIT: 1	B.S.I.: 78200

TITLE: GADOLINIUM BY ARSENAZO III	PROCEDURE NO.: 78200-AP-GA1	REV.: 12

<u>**POINT LEPREAU GENERATING STATION**</u>

<u>**CHEMISTRY LABORATORY ANALYTICAL PROCEDURE**</u>

<u>**GADOLINIUM ARSENAZO III**</u>

<u>**78200-AP-GA1**</u>

Issued By: _____ Date: _____

PREPARED BY: K. MacGibbon	DATE: 02-08-14	REVIEWED BY: R. Culligan	DATE:	APPROVED BY: G.H. Brown	DATE:	PAGE: 1 of 16

REVISION RECORD

AUTHOR	REV	DESCRIPTION	DATE
	0	Initial Issue	
W. Mawhinney	1	Not Tracked	Oct./91
W. T. Underhill	2	- Revised to incorporate 3 point calibration. - Quality Control Standard verification and calibration linearity checks added. - Added tables for sample dilutions. Added precision statistics for aliquots between 0.200 and 0.300 mg Gd/L H_2O. - Added detection limits based on INPO criteria. - Incorporated use of Quality Control Report Form.	July/97
W. T. Underhill	3	- Added requirement to verify calibration standards and Quality Control standards per 1-78200-QC-01. - Changed volume of ARSENAZO III solution from 1.0 ml to 2.0 ml. - Changed dilution factor for Moderator Poison tank samples. - Added precision statistics for aliquots between 0.100 and 0.200 mg Gd/L H_2O.	Aug./97
W. T. Underhill	4	- Changed calibration standards to 0.100, 0.200 and 0.300 mg GD/L H_2O. - Added computer calculation procedure and report form. - Revised result reporting criteria (Sect. 5.2#2). - Changed QC Check Standard from 9000 to 10000 mg Gd/L H_2O. - Revised precision statistics and detection limits. - Added references.	Oct./97
W. MacKeigan	5	- Added references to use of new Varian Cary 1C UV/VIS Spectrophotometer. - Deleted manual calculation section. - Added requirement to cool standards to 25°C. - Removed requirement to zero the Reagent Blank Absorbance. - Deleted upper limit on calibration slope. - Added Revision Record.	April/98

CHEMISTRY DEPARTMENT

Point Lepreau G.S.				
FUNCTION: ANALYTICAL PROCEDURE	SYSTEM: CHEMISTRY LABORATORY		UNIT: 1	B.S.I.: 78200
TITLE: GADOLINIUM BY ARSENAZO III		PROCEDURE NO.: 78200-AP-GA1		REV.: 12

REVISION RECORD (Cont'd)

AUTHOR	REV	DESCRIPTION	DATE
K. MacGibbon	6	- Changed mgGd/Kg to mgGd/Kg. - Section 4.0 – Deleted reference to DMS200 and added reference to CARY50. - Section 8.0 – Added reference to the w:\Chemical\Forms directory for location of report form. - Section 10.0 – Added note to divide LLD and MDL by 1.105 to account for density of D_2O. - Added shelf life of 1 month for arsenazo reagent.	Oct/99
K. MacGibbon	7	- Section 2.0 made reference to control charts. - Section 5.2 - added requirement to verify prepared standards if control charts are not used for validating calibration. - Section 6.0 – Removed preparation steps for low concentration standards, removed requirement to verify prepared standards. - Section 7.1 – Added requirement to prepare working calibration and Q.C. check standard. Changed Q.C. check standard dilution factor from 40000 to 50000. - Section 7.2 – Deleted requirement to repeat analysis if sample absorbance is less than 0.200 ppm standard. - Section 8.1.3 made reference to control chart, deleted reference to report form limits. Appendix 1 deleted lower and upper limits on report form.	Mar/00
K. MacGibbon	8	- Section 6 – Minor changes to Arsenazo reagent preparation.	Feb/01
K. MacGibbon	9	- Section 7.2 – Changed step 4 to zero spectrometer on the blank, not nanopure water. Changed step 5 to use standard #1 as the first standard in the calibration set. Changed sample stabilization time to 10 minutes from 5 minutes. - Section 7.2.2 - Changed step 4 to zero spectrometer on the blank, not nanopure water. Changed step 5 to use standard #1 as the first standard in the calibration set. Changed sample stabilization time to 10 minutes from 5 minutes.	Apr/01

REVISION RECORD (Cont'd)

K. MacGibbon	10	- Section 6.0 – Changed Step 3 to 0.05% not 0.1% of arsenazo III solution and 1.0 g to 0.5 g of arsenazo III. - Section 7.1, table 1 – added Std labels to flask numbers 2, 3 & 4. - Section 7.2, step 5 – clarified step to indicate that spectrometer must be zeroed on the blank. Added note to indicate that blank value in not recorded.	June 02
K. MacGibbon	11	- Section 7.2.2 – renumbered to Section 7.3. - Section 7.3 – Changed Steps 4 – 7.	June 02
K. MacGibbon	12	- Section 7.2.1 – Changed Table 2 sample volume for Moderator Poison Tk3 to 1.0 ml from 1.5 ml.	Aug. 02

	CHEMISTRY DEPARTMENT		
Point Lepreau G.S.			

FUNCTION: ANALYTICAL PROCEDURE	SYSTEM: CHEMISTRY LABORATORY	UNIT: 1	B.S.I.: 78200
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Point Lepreau G.S.

1.0   INTRODUCTION

Gadolinium is injected as a solution of gadolinium nitrate into the Moderator System for reactivity control and for reactor shutdown.

This procedure shall be used to determine the concentration of gadolinium in samples from the Main Moderator System, Moderator Auxiliaries, Moderator D2O cleanup and special safety system SDS#2 (LISS). It will also be used for the verification of gadolinium standards.

2.0   OUTLINE OF METHOD

Arsenazo III is a dye that forms a colored complex with gadolinium in an acidic solution at pH 3. This procedure outlines the method for analysis of these solutions using either the Varian Cary 50 UV/VIS or Varian Cary 1C UV/VIS. spectrophotometer. The optimum absorbance for analysis of solutions containing this complex occurs at a wavelength of 653 nanometers.

This procedure is linear up to an aliquot gadolinium concentration of 0.300 mgGd/Kg H_2O. Standard aliquots are prepared and analyzed at concentrations of 0.100 mgGd/Kg H_2O, 0.200 mgGd/Kg H_2O, and 0.300 mgGd/Kg H_2O. A linearity check of the standard absorbances is required. All samples analyzed must be diluted such that the sample absorbances are within the range of absorbances corresponding to the standards.

A Quality Control (Q.C.) check standard will be analyzed with each sample run. The result of the Q.C. check standard must be within control chart criteria limits for the process sample result(s) to be valid, refer to 78200-QM-01.

All absorbances and calculated values shall be recorded on report form #REP-78200-AP-14.1. An example of this form is included in Appendix I of this procedure.

3.0 INTERFERENCES

The reaction is not very selective. All elements reacting with arsenazo III act as inhibitors when the pH at which they are hydrolyzed is lower than the pH at which gadolinium begins to hydrolyze.

The following substances do not act as inhibitors in quantities up to 200 mg/kg: Aluminum, iron, sodium, potassium, magnesium, sulfate, chloride and phosphate. Boron does not interfere at concentrations up to 1000 mg/kg. Nitrate does not interfere in low concentrations.[2]

4.0 APPARATUS

7829-EQ47: Varian Cary 1C UV-Visible Spectrophotometer
7829-EQ50: Varian Cary 50 UV-Visible Spectrophotometer
Cell, 1 cm flow-thru (visible)
Volumetrics Flasks, 100 mL, 500 mL, and 1000 mL; Beaker, 250 mL
Calibrated Pipettes, 0.5 mL and 1 mL
Oxford Pipettetor (or equivalent)
Hot plate & stirrer; Filter paper, Whatman 41; Drying oven
PC with Microsoft Excel as well as Report File (R_AP1401.xls) loaded

5.0 PRECAUTIONS

5.1 Personnel Precautions

1.   Process samples will be highly tritiated. All applicable radiation protection procedures must be followed.

2.   Concentrated nitric acid is used, appropriate chemical protection is required.

5.2   Procedural Precautions

1.   The procedure is linear to 0.300 mgGd/Kg H2O. The best precision is obtained using sample aliquots in the range of 0.200 mgGd/Kg H2O to 0.300 mgGd/Kg H2O.

Do not report results from aliquots with absorbance values higher than the absorbance corresponding to the 0.300 mgGd/Kg H2O standard.

2.   Do not report numerical results lower than the Method Detection Limit (MDL). For results between the Lower Limit of Detection (LLD) and the MDL, quote the results as "Detected". Results lower than the LLD shall be quoted as "Not Detected".

3.   Care must be taken during standard preparation to ensure all gadolinium oxide is transferred when using multiple flasks.

4.   Arsenazo III does not dissolve totally. Ensure reagent is filtered. Some variation may occur between batches as observed by blank absorbance.

5.   Always transfer standard solutions from their containers into a beaker prior to Pipetteing. Do not pipette any standard solution directly from the storage bottle.

6.   Calibration and Q.C. check standards must be verified using 78200-QC-01 if control charts are not used to validate calibrations.

6.0   <u>**REAGENTS**</u>

1. **Gadolinium standard solution (Primary Calibration), 1000 mgGd/KgH$_2$O**
    Use a N.I.S.T. grade standard (Mat'l No. 00001708)
    <div align="center"><u>**OR**</u></div>
    Weigh out 1.1526 g of Gd$_2$O$_3$ (dried at 105°C for 2 hours) into a 250 mL beaker. Add 150mL of 2 N HNO$_3$. Heat and stir until dissolved (do not boil). Allow to cool to 25°C. Carefully transfer to a 1000 mL volumetric flask. Ensure all solution is transferred by rinsing the beaker thoroughly with nanopure water. Dilute to 1000 mL using nanopure water. Transfer to a Nalgene bottle and label with the date prepared.

    <u>**Note**</u>**: This standard must have a different lot # than primary Q.C. standard.**

2. **Gadolinium standard solution (Primary Q.C.), 10000 mgGd/KgH$_2$O**
    Use a N.I.S.T. grade standard (Material No. 00001755)
    <div align="center"><u>**OR**</u></div>
    Weigh out 11.526 g of Gd$_2$O$_3$ (dried at 105°C for 2 hours) into a 250 mL beaker. Add 150mL of 2 N HNO$_3$. Heat and stir until dissolved (do not boil). Allow to cool to 25°C. Carefully transfer to a 1000 mL volumetric flask. Ensure all solution is transferred by rinsing the beaker thoroughly with nanopure water. Dilute to 1000 mL using nanopure water. Transfer to a Nalgene bottle and label with the date prepared.

    <u>**Note**</u>**: This standard must have a different lot # than primary calibration standard.**

3. **Arsenazo III solution, 0.05 %** - Dissolve 0.5 g of arsenazo III in 1000 mL of nanopure water. Filter solution through Whatman 41 filter paper. Record shelf life as 1 month.

4. **Buffer solution** - Dissolve 10.21 g of potassium hydrogen phthalate in 500 mL of nanopure water. Add 223 mL of 0.1 N HCl.

5. **Nitric acid, 2 N** - Dilute 126 mL of ACS Grade Conc. HNO$_3$ to 1 L.

6. **Hydrochloric acid, 0.1 N** - Dilute 8.2 mL of ACS Grade Conc. HCl to 1 L.

7.0   **PROCEDURE**

7.1   Preparation of Standards and Q.C. Check Sample

1.   Open the appropriate method file for the UV/Vis spectrometer used. Refer to 78200-IP-47 or 78200-IP-52.

2.   Label each of the required 100 mL volumetric flasks as per Table #1:

TABLE #1

Flask #	Contents
1	BLANK
2	0.100 mgGd/Kg H_2O STANDARD (Std 1)
3	0.200 mgGd/Kg H_2O STANDARD (Std 2)
4	0.300 mgGd/Kg H_2O STANDARD (Std 3)
5	Q.C. CHECK SAMPLE (0.20 mg/Kg)
6	PROCESS SAMPLE #1
7	PROCESS SAMPLE #2
8 etc.	PROCESS SAMPLE # etc.

3.   Pipette 2.0 mL of arsenazo III solution <u>and</u> 10 mL of buffer solution into each 100 mL volumetric flask.

4.   Prepare a 10.0 mgGd/Kg H_2O working calibration standard by pipetting 1.0 mL of the 1000 mgGd/Kg H_2O primary calibration standard into a 100 mL volumetric flask. Dilute to the mark with nanopure water.

5.   Pipette 1.0 mL of 10 mgGd/Kg H_2O working calibration standard into Flask #2 to obtain a 0.100 mgGd/Kg H_2O standard.

6.   Pipette 2.0 mL of 10 mgGd/Kg H_2O working calibration standard into Flask #3 to obtain a 0.200 mgGd/Kg H_2O standard.

7.   Pipette 3.0 mL of 10 mgGd/Kg H_2O working calibration standard into Flask #4 to obtain a 0.300 mgGd/Kg H_2O standard.

7.1   Preparation of Standards and Q.C. Check Sample (Cont'd)

8.   Prepare a 10.0 mgGd/Kg working Q.C. check standard by pipetting 1.0 mL of the primary Q.C. check standard into a 1000 mL volumetric flask. Make up to 1000 mL using nanopure water.

9.   Pipette 2.0 mL of the working Q.C. check standard from the 1000 mL flask (prepared in Step 7.1.7) into Flask #5. (**Note**: Dilution Factor D.F. = 50000).

7.2   Preparation and Analysis of Samples

7.2.1   SDS#2 (LISS), and Moderator Liquid Poison Samples

1.   For SDS#2 (LISS) Samples & 10000 mg/kg Q.C. Standards, Pipette 1.0 mL of sample into a 1000 mL volumetric flask. Make up to 1000 mL using nanopure water.

For Moderator Liquid Poison Samples and 1000 mg/kg Standards, Pipette 1.0 mL of Process Sample into a 100 mL volumetric flask. Make up to 100 mL using nanopure water.

2.   Use the guidelines in Table #2 to Pipette a suitable volume of process sample from the 1000 mL or 100 mL flask prepared in Step 7.2.1.1 into flask #6, #7, etc. as required.

TABLE #2

PROCESS SYSTEM	VOLUME (mL)	DILUTION FACTOR (D.F.)
SDS#2 (LISS)	2.5	40000
Moderator Poison TK3	1.0	10000
*1000 mg/kg Standard Verification	2.5	4000

3.   Add nanopure water to all aliquot flasks to the 100 mL mark.

4.   Stopper and mix well. Allow 10 minutes for complete reaction.

7.2   Preparation and Analysis of Samples (Cont'd)

5.   Zero the spectrophotometer using the blank solution.

Note: If using the Cary 50, prior to starting the method (clicking the 'Start' button) ensure the dip probe is in the blank solution. Do not record the absorbance value for the blank, it is recorded on the report form as 0.000.

6.   Analyze Flask #2 (Std #1). **RECORD** the absorbance of Standard #1 on the report form.

7.   Analyze the contents of the remaining flasks. **RECORD** all absorbance values on the report form.

8.   Calculate results as per Section 8 of this procedure. Attach the spectrophotometer printer output to the report form.

7.3   Main Moderator Samples (Less than 20 mgGd/Kg D_2O)

1.   Use the guidelines in Table #3 to Pipette a suitable volume of process sample into Flask #6, #7, etc. as required.

TABLE #3

EXPECTED SAMPLE CONCENTRATION (mgGd/Kg D_2O)	VOLUME (mL)	DILUTION FACTOR (D.F.)
< 0.3	88	1.136
1	20	5
2	10	10
3 - 5	5.0	20
5 - 9	3.0	33.3
9 - 13	2.0	50
13 - 18	1.5	66.7
18 - 20	1.0	100

CHEMISTRY DEPARTMENT

Point Lepreau G.S.

FUNCTION:	SYSTEM:	UNIT:	B.S.I.:
ANALYTICAL PROCEDURE	CHEMISTRY LABORATORY	1	78200

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7.3   <u>Main Moderator Samples (Less than 20 mgGd/Kg D$_2$O)</u>   (Cont'd)

    2.   Add nanopure water to all aliquot flasks to the 100 mL mark.

    3.   Stopper and mix well. Allow at least 10 minutes for complete reaction.

    4.   Zero the spectrophotometer using the blank solution.

    <u>**Note:**</u> **If using the Cary 50, prior to starting the method (clicking the 'Start' button) ensure the dip probe is in the blank solution**. Do not record the absorbance value for the blank, it is recorded on the report form as 0.000.

    5.   Analyze Flask #2 (Std #1). **RECORD** the absorbance of Standard #1 on the report form.

    6.   Analyze the contents of the remaining flasks. **RECORD** all absorbance values on the report form.

    7.   Calculate results as per Section 8 of this procedure. Attach the spectrophotometer printer output to the report form.

8.0   **<u>CALCULATIONS</u>**

8.1   <u>Calculation Using Computer</u>

8.1.1   Load Excel and open the spreadsheet file named R_AP1401.xls from the W:\ChemicalForms directory. If the network is unavailable, load the form from the C:\REPFORMS directory on the local computer.

8.1.2   Enter the absorbance values, sample I.D.'s, and dilution factors into the shaded cells.

8.1   Calculation Using Computer (Cont'd)

8.1.3   The Q.C. standard result and the process results will be automatically calculated. **Analytical results cannot be used if control chart criteria is not met.**

Record process sample results in the lab database, and other applicable worksheets. Print the completed REP-78200-AP-14.1 form and forward to lab Q.C. senior.

9.0   PRECISION

The precision of this procedure has been determined to be as follows:

For Aliquot Concentrations between 0.2 mgGd/Kg H_2O and 0.3 mgGd/Kg H_2O:

95.0 % confidence level: (1-tail)	2.6 %
95.0 % confidence level: (2-tail)	3.1 %
99.9 % confidence level: (1-tail)	5.0 %
99.9 % confidence level: (2-tail)	5.3 %

For Aliquot Concentrations between 0.1 mgGd/Kg H_2O and 0.2 mgGd/Kg H_2O:

95.0 % confidence level: (1-tail)	5.1 %
95.0 % confidence level: (2-tail)	6.1 %
99.9 % confidence level: (1-tail)	9.8 %
99.9 % confidence level: (2-tail)	10.5 %

For Aliquot Concentrations between the MDL and 0.1 mgGd/Kg H_2O:

95.0 % confidence level: (1-tail)	22.4 %
95.0 % confidence level: (2-tail)	26.8 %
99.9 % confidence level: (1-tail)	43.1 %
99.9 % confidence level: (2-tail)	46.1 %

CHEMISTRY DEPARTMENT

Point Lepreau G.S.

FUNCTION:	SYSTEM:		UNIT:	B.S.I.:
ANALYTICAL PROCEDURE	CHEMISTRY LABORATORY		1	78200

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10.0 METHOD DETECTION LIMIT

The LLD for this procedure is 0.011 mgGd/Kg H_2O, and the MDL is 0.022 mgGd/Kg H_2O. (INPO criteria)

Note: Divide the above LLD and MDL by 1.105 for detection limits in D_2O.

11.0 REFERENCES

1. Method Validation File No. MV-78200-AP-14.

2. Memo "Verification Of Gadolinium By Arsenazo III Procedure" W.R. Mahwinney to C.K. MacNeil; February 22, 1982; File No. 87-78200.

APPENDIX I: Example of Form # REP-78200-AP-14.1

Analytical Procedure Quality Control Report Form　　　　　　**REP-78200-AP-14.1**
(ref. 1-78200-AP-14 Rev. 06)

PROCESS SYSTEM: (circle)	LISS TANK # 1 2 3 4 5 6 11 13		LIQUID POISON TK 3	MODERATOR Main IX 1 2 3 4 5 Other

PROCEDURE SECTION	FLASK	ABSORBANCE	CONTENTS	
ABSORBANCE VALUES 7.2.1 / 7.2.2	1		0.000 mGd/Kg D_2O BLANK	
	2		0.100 mGd/Kg D_2O STANDARD	
	3		0.200 mGd/KgH$_2$O STANDARD	
	4		0.300 mGd/Kg D_2O STANDARD	
	5		Q.C. CHECK SAMPLE	Dilution Factor=
	6		SAMPLE I.D	Dilution Factor=
	7		SAMPLE I.D	Dilution Factor=
	8		SAMPLE I.D	Dilution Factor=
	9		SAMPLE I.D	Dilution Factor=
	10		SAMPLE I.D	Dilution Factor=
	11		SAMPLE I.D	Dilution Factor=
	12		SAMPLE I.D	Dilution Factor=
	13		SAMPLE I.D	Dilution Factor=
	14		SAMPLE I.D	Dilution Factor=
	15		SAMPLE I.D	Dilution Factor=

SLOPE CHECK

8.1.3

CALCULATED SLOPE OF LEAST SQUARES FIT:

SLOPE [　　　　]

SLOPE RESULT: _____　　_____ R^2

Q.C. CHECK STANDARD

8.1.3

ANALYZED Q.C. CHECK STANDARD

[　　　　] mgGd/Kg H2O

Q.C. STANDARD RESULT: _____

RESULT(S) REPORTED

8.1.3

(Standard Verifications)		(Process Samples)	
	mgGd/Kg H$_2$O		mg Gd/kg D_2O
	mgGd/Kg H$_2$O		mg Gd/kg D_2O
	mgGd/Kg H$_2$O		mg Gd/kg D_2O
	mgGd/Kg H$_2$O		mg Gd/kg D_2O
	mgGd/Kg H$_2$O		mg Gd/kg D_2O
	mgGd/Kg H$_2$O		mg Gd/kg D_2O
	mgGd/Kg H$_2$O		mg Gd/kg D_2O
	mgGd/Kg H$_2$O		mg Gd/kg D_2O
	mgGd/Kg H$_2$O		mg Gd/kg D_2O
	mgGd/Kg H$_2$O		mg Gd/kg D_2O

NOTE: Only 3 significant figures are reportable

Completed By: _____　　Reviewed By: _____

Date/Time: _____　　Date/Time: _____