Date Entered: Dec 06, 2000

TO: USNRC/WASHINGTON
JMCKNIGHT Copy Number: 145

TRANSMITAL NUMBER: **170851**

PROCEDURE NUMBER: EI-7.3

TITLE: HYDROGEN ANALYSIS OF POST ACCIDENT SAMPLES

TRANSMITTAL: LISTED BELOW ARE NEW/REVISED PROCEDURES WHICH MUST BE IMMEDIATELY INSERTED INTO OR DISCARDED FROM YOUR PROCEDURE MANUAL.

Action Required	Section or Description
REMOVE AND DESTROY	EI-7.3, R/6, ENTIRE PROCEDURE
REPLACE WITH	EI-7.3, R/6, ENTIRE PROCEDURE
	EDITORIAL

SIGN, DATE, AND RETURN THE ACKNOWLEDGEMENT FORM WITHIN 10 DAYS TO THE PALISADES PLANT DOCUMENT CONTROL.

SIGNATURE OR INITIALS _____ DATE _____

A045

Procedure No EI-7.3
Revision 6
Issued Date 12/6/00

PALISADES NUCLEAR PLANT
EMERGENCY IMPLEMENTING PROCEDURE

TITLE: HYDROGEN ANALYSIS OF POST ACCIDENT SAMPLES

Michael Sellman / 12/6/00
Procedure Sponsor — Date

ILGallagher / 6/3/97
Technical Reviewer — Date

WCEdwards / 7/23/97
User Reviewer — Date

TITLE: HYDROGEN ANALYSIS OF POST ACCIDENT SAMPLES

Table of Contents

TITLE: HYDROGEN ANALYSIS OF POST ACCIDENT SAMPLES

Table of Contents

ATTACHMENTS

Attachment 1, "Baseline Editing"
Attachment 2, "PASM Method"

TITLE: HYDROGEN ANALYSIS OF POST ACCIDENT SAMPLES

USER ALERT
REFERENCE USE PROCEDURE

Refer to the procedure periodically to confirm that all procedure segments of an activity will be or are being performed. Where required, sign appropriate sign-off blanks to certify that all segments are complete.

1.0 PERSONNEL RESPONSIBILITY

The OSC Chemistry Supervisor shall implement this procedure.

2.0 PURPOSE

This document describes the procedural steps necessary to determine the hydrogen concentration from a PCS gas sample collected at the PASM panel. This is a backup method to the in-line GC located in the PASM panel.

3.0 INITIAL CONDITIONS AND/OR REQUIREMENTS

This procedure shall be implemented per Emergency Implementing Procedure EI-7.2, "Emergency Post Accident Analysis."

4.0 REFERENCES

4.1 SOURCE DOCUMENTS

4.1.1 NUREG 0654

4.1.2 NUREG 0737

4.1.3 Technical Specifications Chapter 5, Section 5.5.3, "Post Accident Sampling Program"

e

TITLE: HYDROGEN ANALYSIS OF POST ACCIDENT SAMPLES

4.2 **REFERENCE DOCUMENTS**

4.2.1 Chemistry Procedure CH 4.48, "Gas Composition Analysis Using HP 6890 Gas Chromatograph"

4.2.2 Instruction Manual for Hewlett-Packard 6890 Gas Chromatograph

4.2.3 ASTM Standards, 1982, Volume 42, E26073, "Standard Recommended Practice for General Gas Chromatograph Procedures"

4.2.4 Chemistry Procedure CH 1.5, "Operational Chemistry Logs, Records, Graphs, Labels, and Data Sheets"

4.2.5 Palisades Administrative Procedure 10.46, "Plant Records"

4.2.6 Emergency Implementing Procedure EI-1, "Emergency Classification and Actions"

4.2.7 Emergency Implementing Procedure EI-7.0, "Emergency Post Accident Sampling Decision Process"

4.2.8 Emergency Implementing Procedure EI-7.2, "Emergency Post Accident Analysis"

5.0 **EQUIPMENT AND REAGENTS**

5.1 **EQUIPMENT**

Hewlett-Packard 6890 Gas Chromatograph and computer

5.2 **REAGENTS**

5.2.1 Argon Carrier Gas, 99.995% Ar minimum (High Purity)

5.2.2 Helium Carrier Gas, 99.995% He minimum (High Purity)

5.2.3 Gas Standards, such as Matheson Certified Grade or equivalent. See standardization and functional check sections for specific standards required.

TITLE: HYDROGEN ANALYSIS OF POST ACCIDENT SAMPLES

6.0 PRECAUTIONS AND LIMITATIONS

6.1 PERSONNEL SAFETY

6.1.1 Heavy rubber gloves or remote handling tools may be used when handling radioactive samples to minimize beta exposure to the extremities.

6.1.2 Radioactive samples should not be released to the laboratory atmosphere. Vent samples, gas sampling valves, and carrier gas effluents to proper exhausts.

6.1.3 Gas cylinders may contain high pressure (> 2000 psi). Use care when handling gas cylinders and when opening cylinder valves to avoid damage to regulator and prevent damaging the cylinder valve which may cause personal harm.

6.1.4 The use of heavy gases such as argon and nitrogen should be used in well ventilated environments to prevent O_2 deficient atmospheres.

6.1.5 Care should be used in percent levels of hydrogen and oxygen to prevent ignition.

6.2 INTERFERENCES

6.2.1 Gases other than helium, hydrogen, oxygen, and nitrogen may interfere by producing "late peaks" and may appear to be drift.

6.3 WORKING RANGE

Hydrogen	0% to 0.025% for PASM Diluted PCS Gas Samples

6.4 PROCEDURE PRECAUTION

6.4.1 Carrier gas flow must be established prior to turning ON cell (detector) filament current. The thermal conductivity detector may be destroyed if carrier gas flow is interrupted while the detector is energized.

6.4.2 The same operating conditions must be used for standardization, functional checks and sample analysis. These include: carrier gas flow rate, cell (detector) filament temperature, and column temperature.

TITLE: HYDROGEN ANALYSIS OF POST ACCIDENT SAMPLES

7.0 PROCEDURE

USER ALERT
REFERENCE USE PROCEDURE

Refer to the procedure periodically to confirm that all procedure segments of an activity will be or are being performed. Where required, sign appropriate sign-off blanks to certify that all segments are complete.

NOTE: The steps described in this procedure outline basic methods of performing tasks. Advanced users may consult the vendor manuals for additional methods of performing these same tasks.

7.1 STANDARDIZATION

NOTE: Gas Standards listed are recommended standards, other standards may be used.

7.1.1 Gas Standards, Matheson Certified Grade or equivalent

For hydrogen use ..... 0.025% for PASM Diluted PCS Gas Samples
Balance Nitrogen

NOTE: Attachment 2 may be used as a reference for the analytical method.

7.1.2 Under "Program Manager," place arrow on "HP Chem Station" and double click.

7.1.3 Place arrow on "Instrument 1 Online" and double click.

7.1.4 Place arrow on "File" and click once.

7.1.5 Place arrow on "Load" and click.

7.1.6 Place arrow on "Method" and click once. Do not save current changes.

7.1.7 Place arrow on "PASM.M" and double click.

7.1.8 Using the manual keyboard buttons on the GC, push "Front Det" key.

TITLE: HYDROGEN ANALYSIS OF POST ACCIDENT SAMPLES

7.1.9 Using "▼" key, scroll down to Filament and push "ON" key.

7.1.10 Using the manual keyboard buttons on the GC, push "Back Det" key.

7.1.11 Using "▼" key, scroll to Filament and push "ON" key.

7.1.12 Ensure GC is ready for injection, via the GC status board or looking on the computer for status.

7.1.13 Inject a minimum of 5 cc of calibration gas standard containing approximately 250 ppm hydrogen balance nitrogen into the GC injection port.

7.1.14 Press start on the GC manual keyboard. Wait for analysis to complete.

7.1.15 Place arrow on "View" and click once.

7.1.16 Place arrow on "Data Analysis" and click once.

7.1.17 Place arrow on "File" and click once.

7.1.18 Place arrow on "Load Signal" and click once.

7.1.19 Place arrow on desired file and double click. This will load the file.

7.1.20 Place arrow on "Calibration" and click once.

7.1.21 Place arrow on "Calibrate/Recalibrate" and click once.

7.1.22 Place arrow in circle of "New Table" and click once.

7.1.23 Place arrow on "OK" and click once.

7.1.24 Place arrow on "Yes" and click once.

7.1.25 Place arrow on hydrogen retention time from results of chromatogram and click once. Baselines may be edited as necessary per Attachment 1, "Baseline Editing."

7.1.26 Place arrow in "Compound Box" and click once.

7.1.27 Enter in "Hydrogen" for compound name.

TITLE: HYDROGEN ANALYSIS OF POST ACCIDENT SAMPLES

7.1.28 Place arrow on "Amt %" in desired line and click once.

7.1.29 Enter in desired Amt % concentration of hydrogen calibration standard.

7.1.30 Place arrow on "Nitrogen" retention time from results of chromatograph and click once.

7.1.31 Place arrow in "Compound Box" and click once.

7.1.32 Enter in "Nitrogen" for compound name.

7.1.33 Place arrow on "Amt %" and click once.

7.1.34 Enter in desired Amt % of concentration of nitrogen calibration standard.

7.1.35 Place arrow on "Enter" and click once.

7.1.36 Place arrow on "OK" and click once.

7.1.37 Place arrow on "Yes" and click once to remove excess peaks if asked. Calibration Data Warning may come up, if so, then click on "OK."

7.2 **FUNCTIONAL CHECK**

7.2.1 Under Program Manager place arrow on "HP Chemstation" and double click.

7.2.2 Place arrow on "Instrument/Online" and double click.

7.2.3 Place arrow on "File" and click once.

7.2.4 Place arrow on "Load" and click once.

7.2.5 Place arrow on "Method" and click once.

7.2.6 Place arrow on "PASM.M" and click once.

7.2.7 Using the keyboard on the GC, push "Front Det" key.

7.2.8 Using "▼" key, scroll down to Filament and push "On" key.

7.2.9 Using the keyboard button on the GC, push "Back Det" key.

TITLE: HYDROGEN ANALYSIS OF POST ACCIDENT SAMPLES

7.2.10 Using "▼" key, scroll down to Filament and push "On" key.

7.2.11 Ensure GC is ready for injection via the status board.

7.2.12 Inject a minimum of 5 cc of functional check standard, approximately 100 ppm hydrogen balance nitrogen into GC injection port.

7.2.13 Press "Start" on the GC keyboard.

7.2.14 Edit baselines as necessary per Attachment 1, "Baseline Editing."

7.2.15 Record results of hydrogen and nitrogen functional check standard on the appropriate data sheets when chromatograph is complete.

7.3 SAMPLE ANALYSIS

NOTE: Since a Functional Check is performed daily or prior to use, it is assumed all instrument conditions are correct except for adjustments that may be required for each analysis.

7.3.1 Obtain a gas tight syringe from the PASM cabinet.

7.3.2 With syringe plunger fully inserted, open inlet valve, green button in, red button out.

7.3.3 While gas sample is behind shield, insert needle into serum vial piercing septum of sample bottle.

7.3.4 Retract syringe plunger to 5 cc mark.

7.3.5 Close inlet valve, green button out, red button in.

7.3.6 Retract syringe needle out of sample bottle septum.

7.3.7 Insert syringe needle into GC sample septum.

7.3.8 Open syringe inlet valve, green button in, red button out.

7.3.9 Depress syringe plunger to fully inserted position, injecting sample into GC.

7.3.10 Press "Start" on GC keyboard. Run takes about 10 minutes.

7.3.11 Return syringe to behind shield in hood.

7.3.12 Edit chromatograph as necessary per Attachment 1.

7.3.13 Record % hydrogen results in Section 8.2 of Emergency Implementing Procedure EI-7.2, "Emergency Post Accident Analysis."

7.4 **INSTRUMENT SHUTDOWN**

7.4.1 Using the GC keyboard, press "Front Det" key.

7.4.2 Using "▼" key, scroll down to Filament and press "Off " key.

7.4.3 Using GC keyboard, press "Back Det" key.

7.4.4 Using "▼" key, scroll down to Filament and press "Off" key.

8.0 **CALCULATIONS**

8.1 The HP 6890 requires no calculation by the operator. The computer does the calculation internally and prints out value in %.

9.0 **ACCEPTANCE CRITERIA**

Functional check should be within ± 20% of the actual value.

10.0 **ATTACHMENTS AND RECORDS**

10.1 **ATTACHMENTS**

10.1.1 Attachment 1, "Baseline Editing"

10.1.2 Attachment 2, "PASM Method"

10.2 **RECORDS**

Records generated by this procedure shall be filed in accordance with Palisades Administrative Procedure 10.46, "Plant Records."

11.0 **SPECIAL REVIEWS**

None

BASELINE EDITING

1. Under "Data Analysis," move arrow to "File" and click once.

2. Place arrow on "Load Signal" and click once.

3. Under File Name place arrow on desired file and double click. If peak is extremely small, continue with Step 4. If peak is adequate, go to Step 6.

4. Place arrow on "Graphics" and click once.

5. Place arrow on "Signal Options" and click once. Change Time Range and Response Range values to increase the peak size, and "OK."

   Suggested values:

	Minimum	Maximum
Time Range	2.300	3.000
Response Range	-180.000	1.000

6. Place arrow under chromatograph baseline and to the left of the desired peak to be edited. Hold down left side of mouse and drag across the baseline and up until you get to the entire peak in the box. This will zoom in on your peak of interest.

7. Place arrow on "Integration" and click once.

8. Place arrow on "Draw Baseline" and click once.

9. Place arrow on baseline of chromatogram at the beginning of the peak and hold left side of mouse down. Drag the arrow to the desired end of the peak and release left button on mouse. This will put a white line across the baseline.

10. Place arrow inside the peak and double click. This will redraw the baseline and the white line will disappear.

11. Repeat Steps 4 to 8 for other peaks.

12. When baseline editing is complete, place arrow on "Report" and click once.

13. Place arrow on "Print Report" and click once. This will give you the results of the edited baselines.

PASM METHOD

Method: C:\HPCHEM\1\METHODS\PASM.M of 4/10/97 2:25:32 PM

Method Information

This method is for PASM gas analysis for hydrogen.

Run Time Checklist

Pre-Run Cmd/Macro: off

Data Acquisition: on

Standard Data Analysis: on

Customized Data Analysis: off

Save GLP Data: off

Post-Run Cmd/Macro: off

Save Method with Data: off

==========

HP6890 GC METHOD

==========

OVEN
- Initial temp: 60 'C (On)
- Initial time: 6.50 min
- Ramps:

#	Rate	Final temp	Final time
1	0.0(Off)		

- Post temp: 50 'C
- Post time: 0.00 min
- Run time: 6.50 min
- Maximum temp: 160 'C
- Equilibration time: 0.10 min

FRONT INLET (PURGED PACKED)
- Initial temp: 200 'C (On)
- Flow: 37.7 mL/min (On)
- Gas type: Argon methane 5%

BACK INLET (PURGED PACKED)
- Initial temp: 200 'C (On)
- Flow: 24.7 mL/min (On)
- Gas type: Helium

COLUMN 1
- Packed Column
- Model Number: wasson ???
- Max temperature: 165 'C
- Mode: constant flow
- Nominal initial flow: 37.2 mL/min
- Inlet: Front Inlet
- Outlet: Front Detector
- Outlet pressure: ambient

COLUMN 2
- Packed Column
- Model Number: wasson 1
- Max temperature: 165 'C
- Mode: constant flow
- Nominal initial flow: 23.5 mL/min
- Inlet: Back Inlet
- Outlet: Back Detector
- Outlet pressure: ambient

FRONT DETECTOR (TCD)
- Temperature: 150 'C (On)

BACK DETECTOR (TCD)
- Temperature: 150 'C (On)

PASM METHOD

Method: C:\HPCHEM\1\METHODS\PASM.M of 4/10/97 2:25:32 PM

Reference flow: 37.0 mL/min (Off)
Mode: Constant makeup flow
Makeup flow: 1.0 mL/min (On)
Gas type: Nitrogen
Filament: Off
Negative polarity: Off

Reference flow: 33.0 mL/min (Off)
Mode: Constant makeup flow
Makeup flow: 1.0 mL/min (On)
Gas type: Helium
Filament: Off
Negative polarity: Off

SIGNAL 1
Data rate: 5 Hz
Type: back det - front det
Save Data: On
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 5 Hz
Type: back detector
Save Data: On
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
Derive from front detector

COLUMN COMP 2
Derive from back detector

VALVES
Valve 1 Switching Off
Description:
Valve 2 Switching Off
Description:

POST RUN
Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint
0.01	Valve 1:	On
1.40	Valve 2:	On
2.35	Valve 1:	Off
3.10	Valve 2:	Off

Sequence Recalibration Table

Cal. Line	Cal. Level	Update Response Factor	Update Retention Times	Recalib Interval

PASM METHOD

Method: C:\HPCHEM\1\METHODS\PASM.M of 4/10/97 2:25:32 PM

Integration Event table "Event"

Event	Value	Time
Initial Area Reject	0.000	Initial
Initial Threshold	-1.500	Initial
Initial Peak Width	0.020	Initial
Initial Shoulders	OFF	Initial
Integrator OFF		0.010
Negative Peak ON		1.000
Integrator ON		2.400

Integration Event table "Event_TCD1B"

Event	Value	Time
Initial Area Reject	1.000	Initial
Initial Threshold	-1.000	Initial
Initial Peak Width	0.020	Initial
Initial Shoulders	OFF	Initial
Integrator OFF		0.000
Negative Peak ON		0.100
Integrator ON		2.500

Integration Event table "Event_TCD2B"

Event	Value	Time
Initial Area Reject	1474.183	Initial
Initial Threshold	3.582	Initial
Initial Peak Width	0.049	Initial
Initial Shoulders	OFF	Initial
Negative Peak ON		1.000

Apply Manual Integration Events: No

Specify Report

Destination:	Printer, Screen
Quantitative Results sorted by:	Retention Time
Report Style:	Short
Sample info on each page:	No
Add Chromatogram Output:	Yes
Chromatogram Output:	Portrait
Size in Time direction:	100 % of Page
Size in Response direction:	40 % of Page

Signal Options

PASM METHOD

Method: C:\HPCHEM\1\METHODS\PASM.M of 4/10/97 2:25:32 PM

==========

Include: Axes, Compound Names, Retention Times, Baselines, Tick Marks
Font: Arial, Size: 8

Ranges: Use Ranges	Min Value	Max Value
Time	2.000	4.000
Response		

Multi Chromatograms: Separated, Each in full Scale

==========

Calibration Table

==========

PASM gas analysis

Calib. Data Modified : Monday, April 07, 1997 1:44:23 PM

Calculate : Normalized Percent
Based on : Peak Areas

Rel. Reference Window : 10.000 %
Abs. Reference Window : 0.000 min
Rel. Non-ref. Window : 10.000 %
Abs. Non-ref. Window : 0.000 min
Default Multiplier : 1.000000 (if not set in sample table)
Default Dilution : 1.000000 (if not set in sample table)
Default Sample Amount : 0.000000 (if not set in sample table)
Calculate Uncal. Peaks: No
Partial Calibration : Yes, identified peaks are recalibrated
Correct All RTs : Yes, even for non-identified peaks

Curve Type : Linear
Origin : Ignored
Weight : Equal

Recalibration Settings:
Average Response : Average all calibrations
Average RT : Floating Average New 75%

Calibration Report Options :
Printout of recalibrations within a sequence:
Calibration Table after Recalibration
Normal Report after Recalibration
If the sequence is done with bracketing:
Results of first cycle (ending previous bracket)

Signal 1 : TCD1 B,
Signal 2 : TCD2 B,

PASM METHOD

Method: C:\HPCHEM\1\METHODS\PASM.M of 4/10/97 2:25:32 PM

RT [min]	Sig	Lvl	Amount [%]	Area	Amt/Area	Ref	Grp	Name
2.758	1	1	2.51800e-3	34.22109	7.35804e-5	+		hydrogen
4.077	2	1	99.99748	1.49102e5	6.70665e-4	+		nitrogen