Raman Based Analytical Method and Level Radioactive Waste Process Monitor for Continuous Real-Time Analysis of High

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Raman Monitor for Hanford Tank Waste

A new process monitor system for rapid quantification of multiple constituents and flow parameters in harsh radiochemical aqueous streams developed for on-line and discrete sample analysis was developed.

Continuous real-time monitoring of retrieval composition
- » Immediate status and composition of retrieval
- » Retrieval summary from start of processing

Process monitor benefits process performance
- » cost savings
- » doesn't require personnel involvement to grab samples
- » doesn't interrupt continuous retrieval
- » easily adaptable for variable waste applications

Monitor real-time concentrations of 8 key analytes in the feed
- » NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, AlO_2^-, CO_3^{2-}, CrO_4^{2-}, OH^- **by Raman**
- » Total sodium concentration **by conductivity/density/temperature**

Chemometric Analysis

Retrieval summary

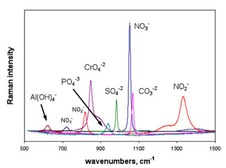
Integrated software

Acceptance Test Criteria Met

20% relative or ±0.5% absolute error

Analyte	%Wt Analytical	Saltpred %Wt Prediction Average	Absolute Range	Relative Error %	Absolute Deviation %Wt	Detection Limit %Wt (M)
A) Early Feed, Total of 2028 Measurements						
NaOH	**4.70**	**4.85** (0.25)	3.8 – 5.9	3.2	0.15	**0.38 (0.09)**
Na_2CO_3	**4.55**	**5.02** (0.13)	4.4 – 5.4	10	0.47	**0.093 (0.009)**
$NaAl(OH)_4$	**4.32**	**4.72** (0.11)	4.4 – 5.1	9.3	0.40	**0.30 (0.025)**
Na_2CrO_4	**0.92**	**0.96** (0.02)	0.92 – 0.99	4.3	0.04	**0.021 (0.001)**
$NaNO_2$	**4.18**	**4.22** (0.04)	4.1 – 4.3	1.0	0.04	**0.19 (0.03)**
$NaNO_3$	**23.82**	**23.47** (0.17)	23.0 – 24.0	1.5	- 0.35	**0.033 (0.004)**
Na_3PO_4	**0.29**	**0.35** (0.04)	0.21 – 0.64	21	0.06	**0.29 (0.02)**
Na_2SO_4	**1.40**	**1.43** (0.01)	1.4 – 1.5	2.1	0.03	**0.047 (0.003)**
Na	**12.75**	**12.87** (0.04)	12.8 – 13.0	1.0	0.12	
B) Late Feed, Total of 779 Measurements						
NaOH	**0.073**	**0.0** (0.29)	0.0 – 1.1		- 0.073	**0.38 (0.09)**
Na_2CO_3	**2.21**	**2.31** (0.04)	2.2 – 2.5	4.5	0.10	**0.093 (0.009)**
$NaAl(OH)_4$	**0.45**	**0.41** (0.03)	0.28 – 0.52	8.9	- 0.04	**0.30 (0.025)**
Na_2CrO_4	**0.26**	**0.19** (0.01)	0.17 – 0.29	27	- 0.07	**0.021 (0.001)**
$NaNO_2$	**0.44**	**0.33** (0.02)	0.23 – 0.41	25	- 0.11	**0.19 (0.03)**
$NaNO_3$	**11.75**	**11.89** (0.10)	11.4 – 12.3	1.2	0.14	**0.033 (0.004)**
Na_3PO_4	**0.78**	**0.75** (0.05)	0.20 – 1.2	3.8	- 0.03	**0.29 (0.02)**
Na_2SO_4	**2.10**	**2.0** (0.02)	2.0 – 2.3	4.8	- 0.10	**0.047 (0.003)**
Na	**5.24**	**5.38** (0.10)	3.9 – 5.9	2.7	0.14	

Raman Spectra of Target Ionic Species in Tank waste

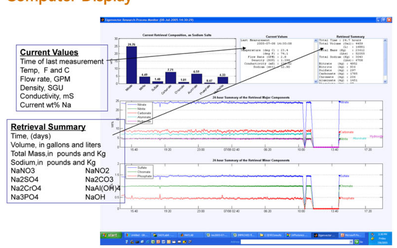


670 nm InPhotonics Inc
15 sec integration time
100 m fiber optic
remote measurements

All instrumentation chemically and radiologically resistant

Flow rate: 0-40 GPM
Caustic feed
Solution density up to 1.5 SPG

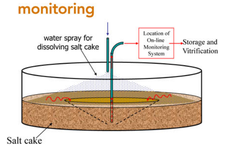
Schematic Presentation of the Software Computer Display



Field Manifold Verification Test

Field Unit calibrated using calibrated laboratory unit

Waste Retrieval from Nuclear Waste Storage Tanks: showing location for on-line process monitoring



Retrieval of single shell tank waste for Hanford bulk vitrification project offers opportunity to deploy on-line monitoring system during dissolving and retrieval of salt cake

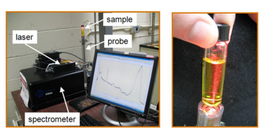
Raman Monitor for Pretreatment Engineering Platform

System QA certified, accepted, and deployed

Predict concentrations of 9 key analytes in sample
- » NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, AlO_2^-, CO_3^{2-}, CrO_4^{2-}, OH^- and $C_2O_4^{-2}$

No sample dilution required
Discrete sample analysis
Measurement performed within full matrix
No sample preparation prior to analysis

Photo of Raman Process Monitor for Discrete Sample Analysis

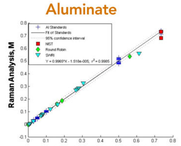


Raman Response Validation

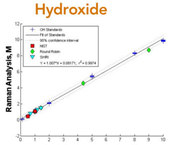
Analyte	Calibration Range, M	Slope	Intercept	R^2	DL M	NIST-traceable standard Molarity, M Certified	Measured	Deviation %
Nitrate	0.04 – 5	10228 ± 173	665 ± 442	0.9989	0.002	0.165	0.159	3.6
Nitrite	0.05 – 5	1070 ± 7	-2 ± 17	0.9998	0.025			
Phosphate	0.04 – 0.2	2169 ± 49	-5 ± 5	0.9985	0.011	0.0915	0.0918	0.3
Sulfate	0.085 – 0.3	13312 ± 12	0.3 ± 1.7	0.9999	0.0014	0.104	0.106	1.9
Carbonate	0.01 – 1.5	3693 ± 32	54 ± 24	0.9998	0.008	0.254	0.259	2.0
Chromate	0.0025 – 0.83	37076 ± 290	-70 ± 111	0.9998	0.0011	0.00756	0.00762	1.0
Aluminate	0.03 – 0.5	1557 ± 22	33 ± 6	0.9988	0.01	0.733	0.761	3.9
Oxalate	0.03 – 0.25	878 ± 16	8 ± 2	0.9987	0.013	0.0109	0.0108	0.7
Hydroxide	0.1 – 10	206 ± 3	5617 ± 15	0.9991	0.044	1.01	1.08	6.7

Raman spectra (20 replicated for each solution) were recorded using a 20 sec integration time at 20±2 °C.

Aluminate

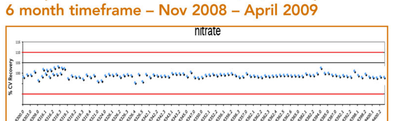


Hydroxide



Comparison of Concentrations obtained by Raman Analysis and Other Analytical Techniques

Example Calibration Verification (CV) trend plot over 6 month timeframe – Nov 2008 – April 2009

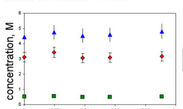


Summary of WTP Raman sample campaign

ASO approved analytical procedure
- » "Raman Analysis of Aqueous Solutions" PNNL Technical Procedure, RPG-CMC-240.
- » HASQARD compliant
- » CAT-2 nuclear facility internal technical review
  - IRC (internal review committee)
  - SME review (subject matter experts)

50 batches of PEP samples analyzed
- » 470 client samples (Nov 2008 – April 2009)
- » Full QA/QC protocol
  - Blanks, matrix spikes, duplicates, calibration verification (initial/final)

Interference Tests



Tested additions of following agents on solutions containing Aluminate, Hydroxide, Nitrate, and Chromate
- » AFA (0 – 0.1 M)
- » Fluoride (0 - 0.2M)
- » MnO_4^- (0 - .02M)
- » Choride (0 – 1M)

Tested effect of adding various agents that could potentially alter response of Raman method.

Results show no effect with addition of AFA, F-, Cl-

Addition of MnO_4^- shows minor effect at highest addition of MnO_4^-.

Spike Recovery

Spike added	% recovery
$Al(OH)_4^-$	98.0
NO_3^-	100.1
CO_3^{-2}	103.3
PO_4^{-3}	95.9
OH^-	109.1
NO_3^-	103.1
$C_2O_4^{-2}$	114.4
CrO_4^{-2}	91.2
SO_4^{-2}	100.4

Each spike added to increase analyte concentration 20-30%.

Spike recovery of 100% is optimum quantitative recovery

+/- 25% spike recovery is acceptable per ASO reporting requirement

Calibration Verification (CV) Recovery

Analyte	CV recovery, %	stand dev
Aluminate	94.7	1.58
Carbonate	101.6	3.70
Chromate	106.0	1.37
Hydroxide	96.3	3.66
Nitrate	99.1	1.33
Nitrite	103.6	2.24
Oxalate	93.9	3.19
Phosphate	94.8	2.28
Sulfate	102.2	0.97

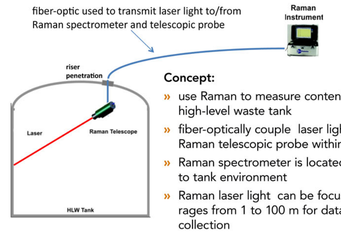
CV sample is fully matrix matched solution containing all analytes

CV measured value of 100% is optimum quantitative recovery

+/- 10% CV recovery is acceptable per ASO reporting requirement

Raman Telescopic Measurements

Telescopic Raman probe being developed for long distance quantitative in-Tank measurement



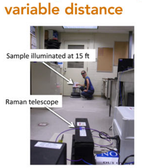
Concept:
- » use Raman to measure contents of high-level waste tank
- » fiber-optically couple laser light to Raman telescopic probe within tank
- » Raman spectrometer is located external to tank environment
- » Raman laser light can be focused at rages from 1 to 100 m for data collection

Candidate Compounds

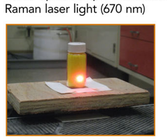
- » Based on tank characterization reports, the following list of compounds have been identified.
- » Raman spectra of these compounds were measured; a data base containing these spectra is being produced.

sample no	formula/name	sample no	formula/name	sample no	formula/name	sample no	formula/name
1	cancrinite	12	$MgSO_4$	23	Fe_2O_3	34	gibbsite
2	$La_2(PO_4)_3$	13	$NaBiO_3$	24	$Fe(OH)_3$	35	$Na_2C_2O_4$
3	$Na_4UO_2(PO_4)_2*3H_2O$	14	$NiNaK(SO_4)_2$	25	$Cr(O)(OH)$	36	Na_2CO_3
4	B_2O_3	15	$AlPO_4$	26	$Cr(OH)_3$	37	$NaZrO_3$
5	$CrPO_4$	16	$CaSO_4$	27	boehmite	38	Na_2SO_4
6	$Ni(OH)_2$	17	$FePO_4$	28	$Ca[Cr(OH)_2PO_4]_2$	39	Na_3PO_4
7	$NaMgPO_7$	18	$BiPO_4$	29	$NaFePO_4$	40	$NaAl(OH)_4$
8	$NaHSO_4$	19	$Cr(NO_3)_3$	30	$FePO_4$	41	$NaNO_2$
9	Na_2HPO_4	20	$Ca(PO_4)_2$	31	$Cr(O)(OH)$	42	$NaNO_3$
10	$Bi(NO_3)_3$	21	Na_3PO_4	32	hydrous		
11	NaH_2PO_4	22	Fe_3O_4	33	sodalite		

Telescopic Raman system measurements at variable distance



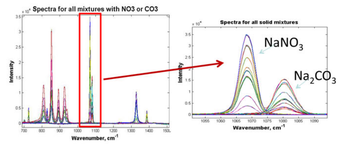
Close-up of sample illuminated with Raman laser light (670 nm)



Sample matrix for telescopic Raman system

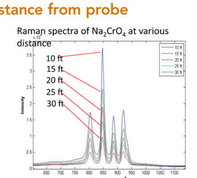
- » 150 individual samples, combinations of 10 components
  - $NaNO_3$, $NaNO_2$, Na_2CO_3, Na_2SO_4, Na_2CrO_4, Na_3PO_4, $Na_2C_2O_4$, $NaAl(OH)_4$, beohmite, and gibbsite.
- » Constructed chemometric data base using all samples at 15 ft
- » Measured a subset of samples at 10, 15, 20, 25, and 30 ft and used for validation of model

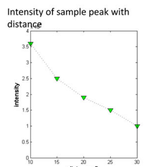
Example of Raman spectra containing variable component mixtures



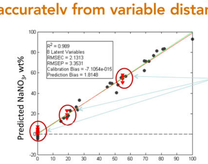
The changes in Raman band location and intensity are used in chemometric model to predict composition of new sample spectrum

Intensity of Raman signal is reduced as a function of distance from probe





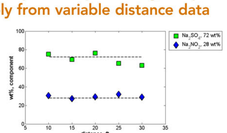
Model is capable of predicting composition accurately from variable distance data



Black symbols, all samples at 15 ft used in model

Red symbols, subset samples, measured at 10, 15, 20, 25, and 30 ft

Model is capable of predicting composition accurately from variable distance data



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