DETERMINATION OF PHOSPHORUS in ASPHALT BINDERS & in BINDERS RECOVERED from BITUMINOUS MIXTURES

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STEP ONE

DEVELOPMENT OF EDXRF ANALYSIS PROCEDURE of ASPHALT to DETERMINE PHOSPHORUS CONTENT

Purpose

- To develop a quick and accurate test method by which percent phosphorus in asphalt could be determined. This could then be used to determine the amount of polyphosphoric acid that was added to an asphalt sample.

Assumptions

- Virgin asphalt does not contain phosphorus
  - Sample tested by DataChem with an ICP was BDL
- Percent phosphorus can be converted back to polyphosphoric acid if the type of acid used is known
  - ex. 115%, 105%, etc.
- Deconvolution software is able to differentiate between S and P peaks

Instrument

- EDXRF
  - Epsilon 5 manufactured by Panalytical with a 600 W Gd-anode X-ray tube and 100kV generator.

Standards

- 27 Standards
  - 4 Base Asphalts
  - 115% Polyphosphoric Acid, Reagent Grade
- S Range: 1.8% to 4.5%
- P Range: 0.00% to 0.54%
  - Conversion to 115% Polyphosphoric Acid: 0.0% to 1.5% Acid in Asphalt

Standard ID	% P	% S
0	0.000	4.15
1	0.544	4.15
2	0.3685	4.15
3	0.284	4.15
4	0.247	4.15
5	0.116	4.15
6	0.0457	4.15
13	0.000	4.52
14	0.000	4.15
15	0.000	4.51
16	0.000	1.81
17	0.0966	1.81
18	0.266	1.81
19	0.219	1.81

Standard ID	% P	% S
20	0.000	3.434
21	0.203	3.434
22	0.322	3.434
23	0.134	3.434
24	0.000	3.369
25	0.170	3.369
26	0.353	3.369
27	0.0588	3.369
28	0.000	4.360
29	0.434	4.360
30	0.0603	4.360
31	0.156	4.360
32	0.306	4.360

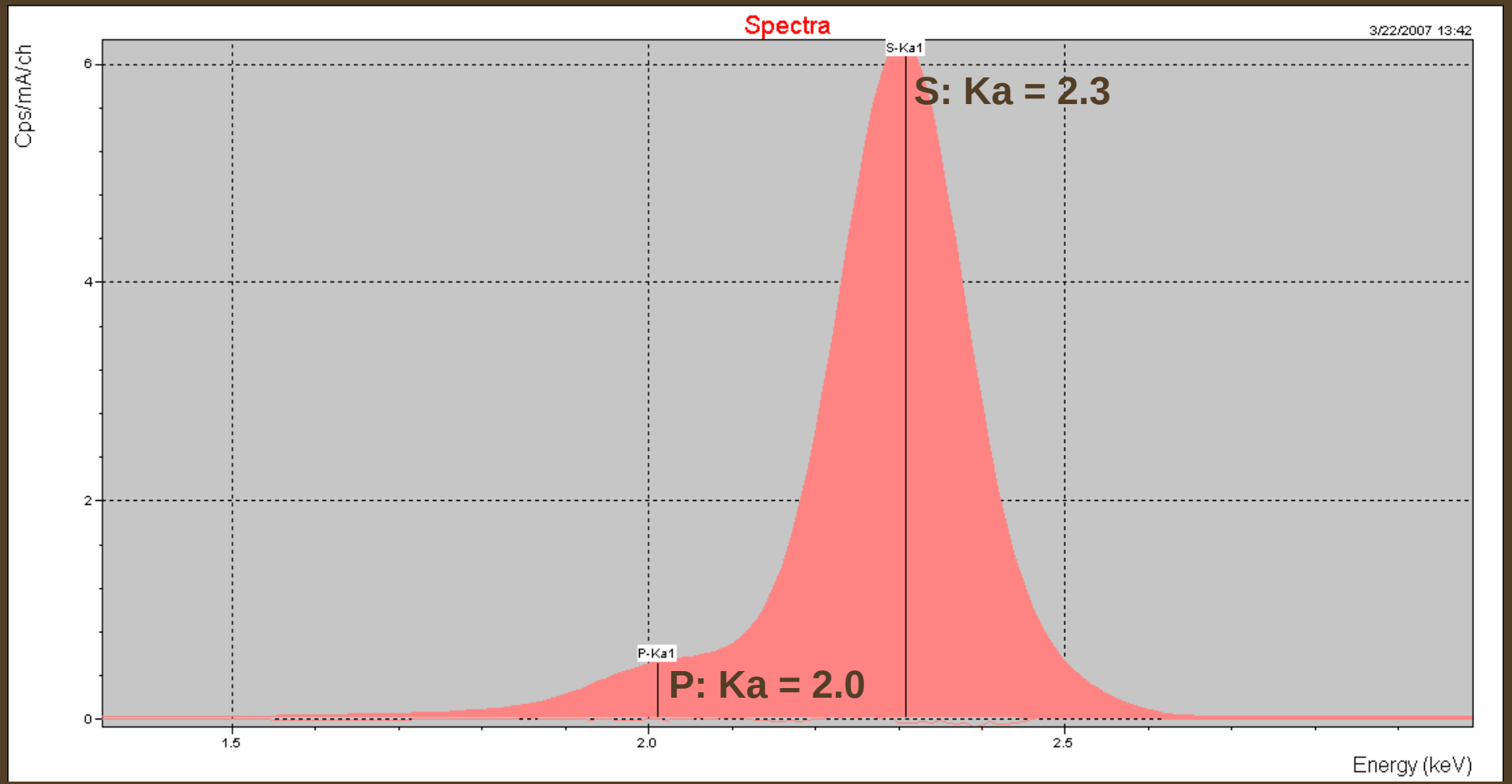
Sample Preparation

Thanks to Olga Puzic for identifying that direct pour can work with Mylar film, although at high enough temperature it will definitely melt

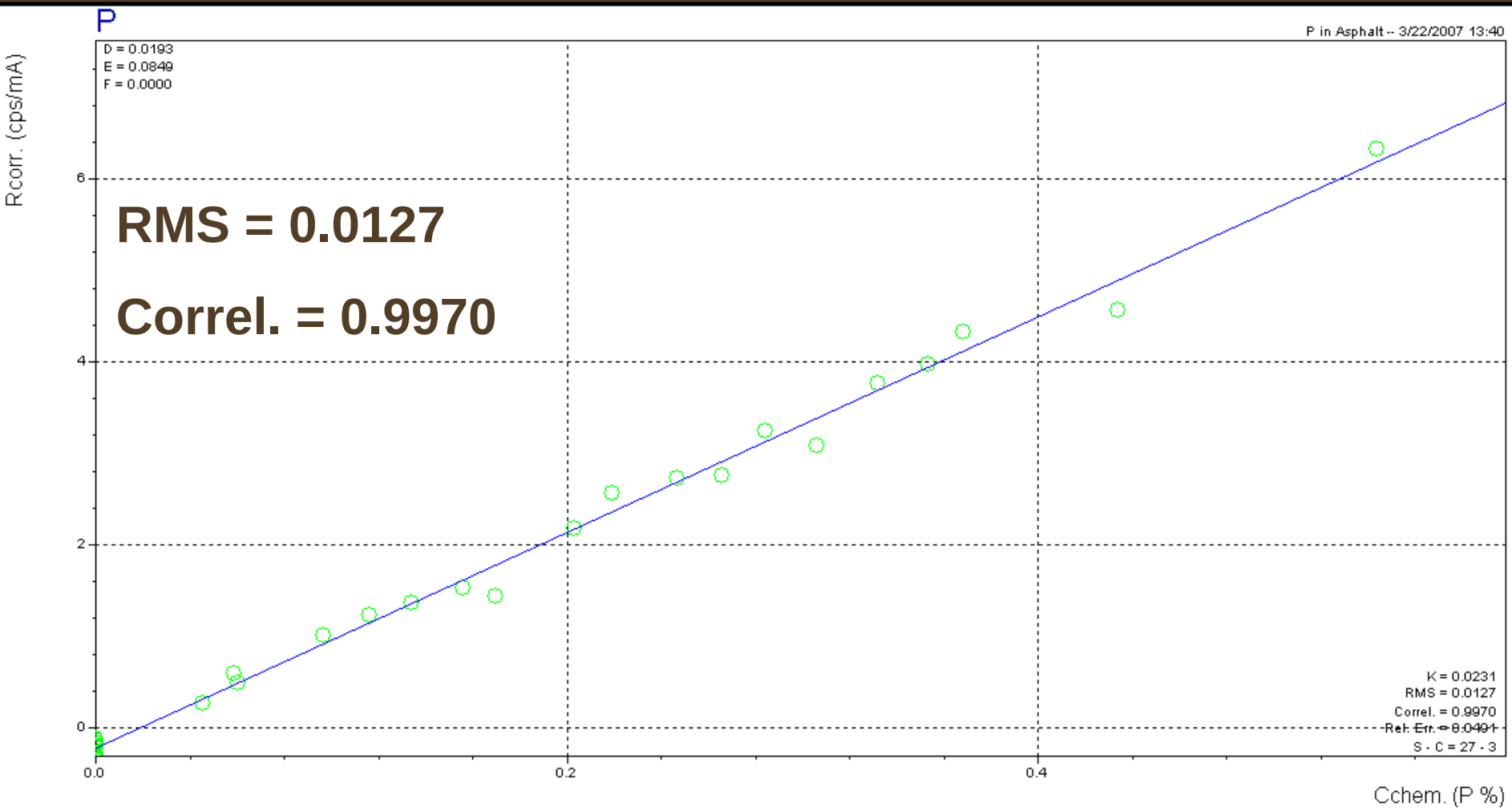
Application

Element	Meas. Time (sec)	Secondary Target	Line
P	600	CaF_2	Ka
S	600	CaF_2	Ka

Deconvolution



P Calibration



Repeatability

- Plant production sample with a calculated formulation target of 0.109% P
- 4.7% higher than target

Run #	% P
1	0.113
2	0.106
3	0.119
4	0.117
Average	0.114
Std Dev	0.0057

ADDITIONAL CONFIRMATORY TEST RESULTS

- Eight samples submitted by Port Authority of New York & New Jersey
- Samples submitted blind
- Technician at Port Authority lab added differing amounts of 105% PPA to samples they received from suppliers. Two suppliers represented
- Data used with permission from PANYNJ

SAMPLE	PG GRADE used to make blend	Wt% P determined	Wt% of 105% PPA reported	Wt% Sulfur	Wt% of 105% PPA reported added by PANYNJ
A	64-22	0.012	No PPA	4.39	0
B	64-22	0.294	0.886	4.29	0.944
C	76-22+SBS	0.116	0.350	4.11	0
D	76-22+SBS	0.333	1.004	4.21	0.645
E	76-22+SBS	0.015	No PPA	4.18	0
F	76-22+SBS	0.105	0.137	4.05	0.371
G	70-22	0.016	No PPA	4.51	0
H	70-22	0.235	0.708	4.30	0.739

Comments from PANYNJ—PPA had partially solidified and some adhered to spatula, somewhat lower result expected. Sample D contained 0.35% PPA according to supplier—0.35%+0.645%=0.995%

STEP TWO

DEVELOPMENT OF PROCEDURES FOR EXTRACTION, RECOVERY AND DETERMINATION OF PHOSPHORUS IN MIXTURES

FOLLOW-UP TESTING

- Sample prepared at a calculated 0.746% of 115% PPA (0.746*0.3631= 0.271% P
- EDXRF result—0.269% P or 0.741% PPA
- MIX TESTING TO BE PERFORMED
  - Use granite, siliceous gravel, limestone aggregates. Mix 6% binder with material finer than 4.76 mm sieve, condition overnight at 100°C
  - Extract, recover the binder. Test for %P in binder
  - Crush recovered aggregate, test for %P and compare to virgin aggregate result

% Phosphorus in Binder Recovered from mix using ambient temperature extraction

0.269% P in original binder	Cisler/granite	Wimmie/siliceous gravel	Waldenberger/limestone
% Phosphorus in 64-28 binder as determined by EDXRF	0.269%	0.269%	0.269%
n-Propyl Bromide #1	0.103%	0.211%	0.149%
n-Propyl Bromide #2	0.073%	0.160%	0.177%
85% Toluene & 15% Ethanol	0.029%	0.151%	0.017%

% Phosphorus Recovered by Extraction

	Cisler/granite	Wimmie/siliceous gravel	Waldenberger/lime stone
% Phosphorus in 64-28 binder as determined by EDXRF	0.269%	0.269%	0.269%
n-Propyl Bromide #1	38.3%	78.4%	55.4%
n-Propyl Bromide #1	27.1%	59.5%	65.8%
85% Toluene & 15% Ethanol	10.8%	56.1%	6.3%

ADDITIONAL EXTRACTION TESTS

Binder used to make mixes contained C 1.32 kPa @ 64°C	% P in recovered binder after 1 extraction	% P in recovered binder after 2 extractions
THF Extracted granite agg	0.088% P equals 32.7% recovery	0.122% P Equals 45.3% recovery 1.88 kPa @ 64°C
THF extracted limestone agg	0.102% P equals 37.9% recovery	1.77 kPa @ 64°C

Appears as though THF is no more effective as a primary extraction solvent than n-Propyl Bromide

WATER SOAK OF RECOVERED AGGREGATE

- Soaked granite agg from toluene ethanol extraction in distilled water @ 60°C
  - % P in water = 0.029% in 100 ml
  - % P in water from virgin granite soaked in water = 0.024% in 100 ml
- Soaked limestone aggregate from THF extraction in distilled water @ 60°C
  - % P in water = 0.019% in 150 ml
  - % P reading in distilled water = 0.014%
- Would appear that soaking has little if any effect on removing P from aggregate

ATTEMPS AT MORE QUANTITATIVE DETERMINATION

- Determined %P in each aggregate prior to mixing with binder
  - Granite—1.67%
  - Gravel—1.096%
  - Limestone—0.344%
- Determined %P in each aggregate after extraction, a total of 300 g aggregate was mixed with 19 g AC treated with 0.75% PPA by wt which provides 19*.0075*.3674= 0.052 g P
  - Granite—1.78% (.0178-.0167)*300=0.33 g P
  - Gravel—1.031% which yields negative P
  - Limestone—0.725% = 1.143 g P

SECONDARY EXTRACTION OF RECOVERED AGGREGATE

- PROCEDURE FOLLOWED
  - Recovered aggregate was further extracted with THF
  - filtered and centrifuged to remove fines
  - THF evaporated with heat lamp
  - Residue solubilized in n-Propyl Bromide (nPB) and added to virgin asphalt sample
  - Flashing nPB from molten asphalt presents some spattering issues, however less dangerous than flashing THF into molten asphalt

- n-Propyl Bromide extraction #2 of granite aggregate yielded 0.073% P or 0.0138 g of P in 19 grams of binder
- THF used to perform a secondary extraction. THF evaporated, residue solubilized in n-propyl bromide and flashed into 24.8 g of binder
  - % P in this binder was 0.138% or 0.034 g of P
- Total wt of Phosphorus = 0.048 g or a total recovery of 92% (.048/0.0518)

SUMMARY & FURTHER WORK

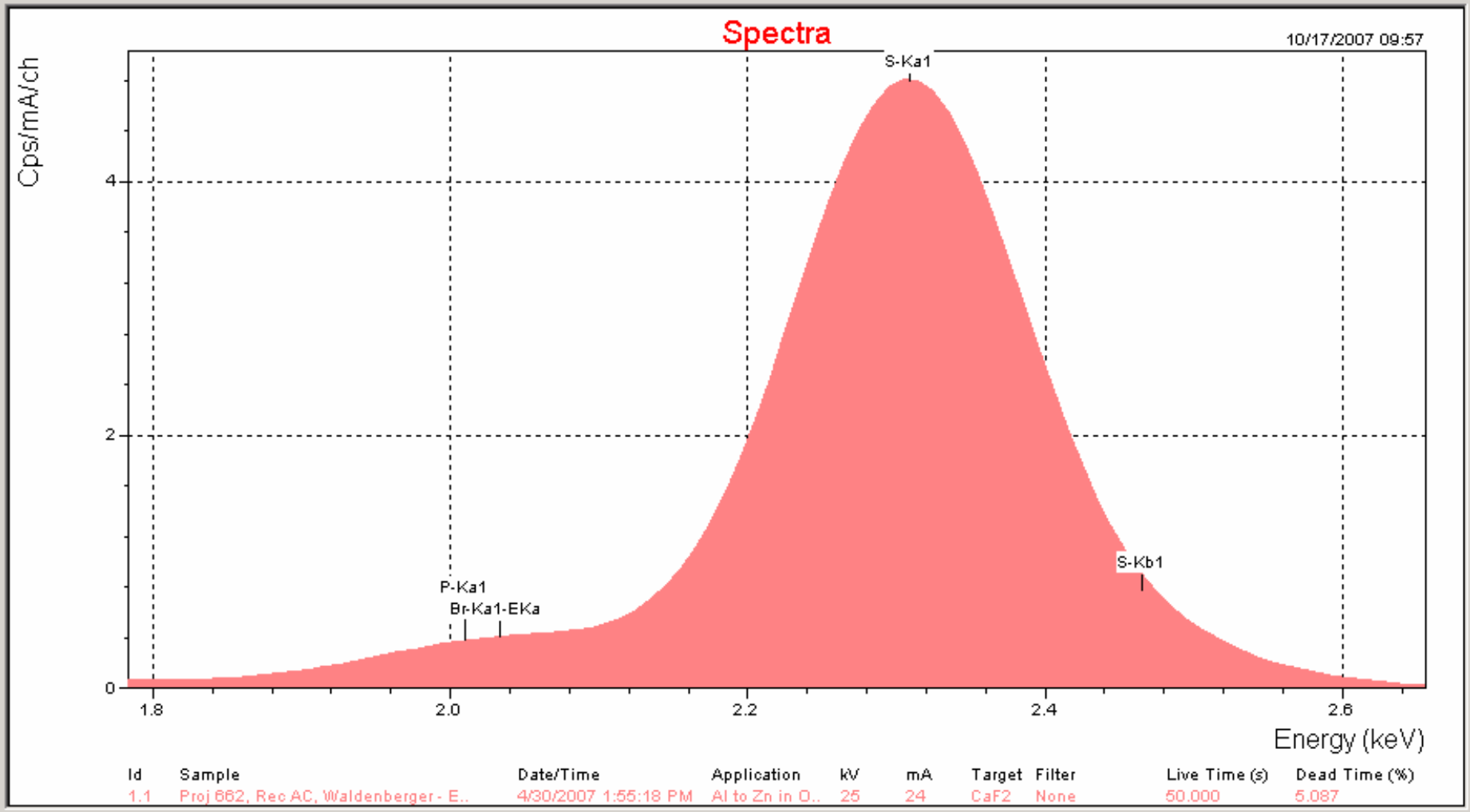
- Secondary or tertiary extraction of extracted aggregate can lead to greater recovery of phosphorus from mixes produced with PPA modified binders
  - This work needs more follow-up testing
- Future extraction work using Soxhlet extractor of mixes with refluxing solvent to determine if this method can lead to greater phosphorus recovery

THREE CORES RECEIVED FROM PORT AUTHORITY OF NEW YORK & NEW JERSEY TO BE TESTED FOR PHOSPHORUS CONTENT

MIX EXTRACTED WITH n-PROPYLBROMIDE IN SOXHLET EXTRACTOR AND RECOVERED WITH ROTOARY EVAPORATOR

		Theoretical
	0.291	
Core 11	0.261	0.72
Virgin aggregate	1.458%	NA

APPEARS AS THOUGH THE SOLVENT IS REMOVING PHOSPHORUS FROM THE AGGREGATE



For germanium the escape peak is 9.87 keV left of the parent peak. Bromine is 11.907 keV which means the the escape peak is at 11.907-9.87=2.037 Phosphorus is 2.013 keV. Escape peak is 1% of the parent peak, which is I begin with.

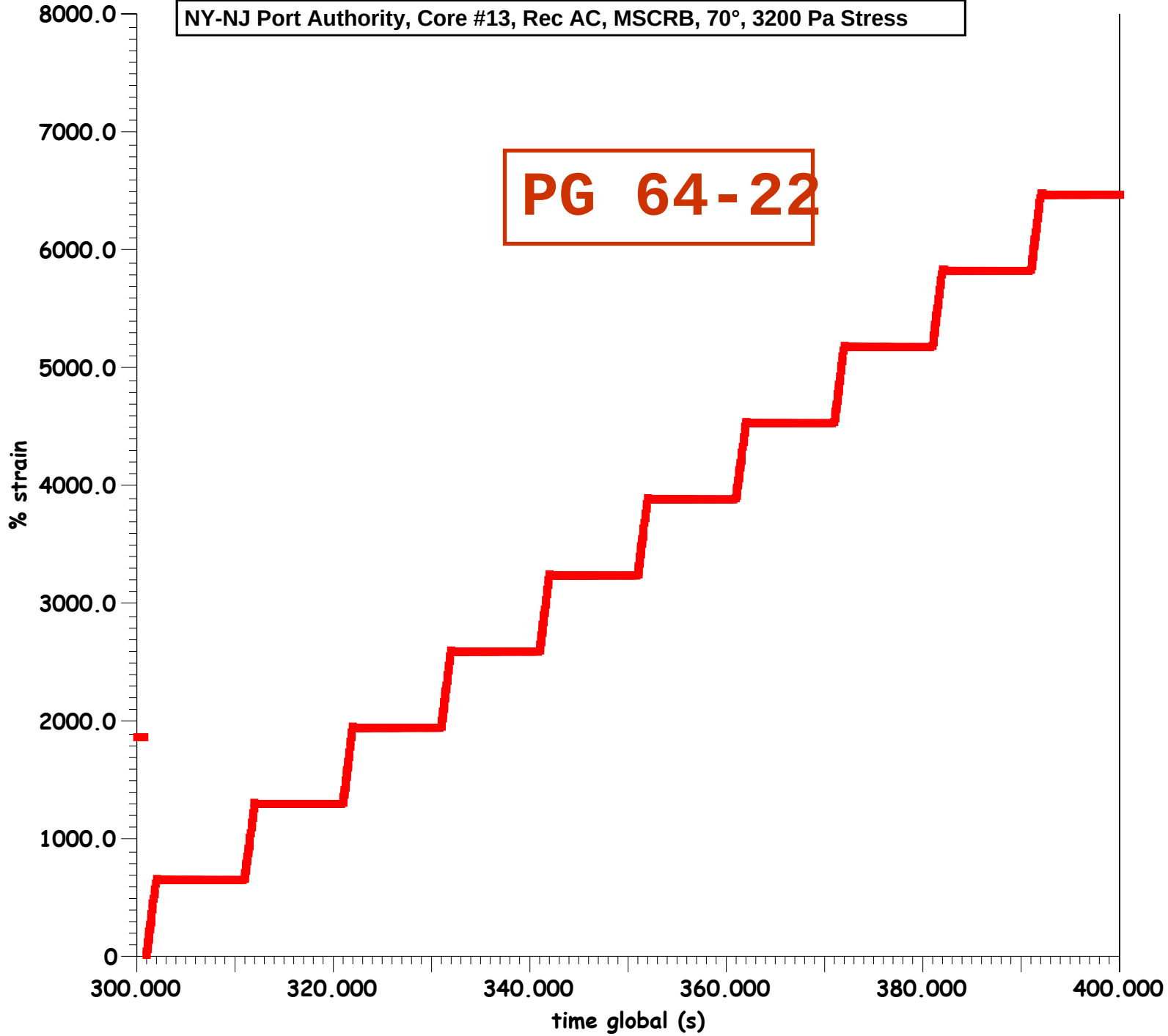
AGGREGATE RECEIVED FROM PORT AUTHORITY WAS MIXED WITH CONTROL BINDERS AND EXTRACTED WITH TRICHLOROETHYLENE AND RECOVERED FOR PHOSPHORUS DETERMINATION

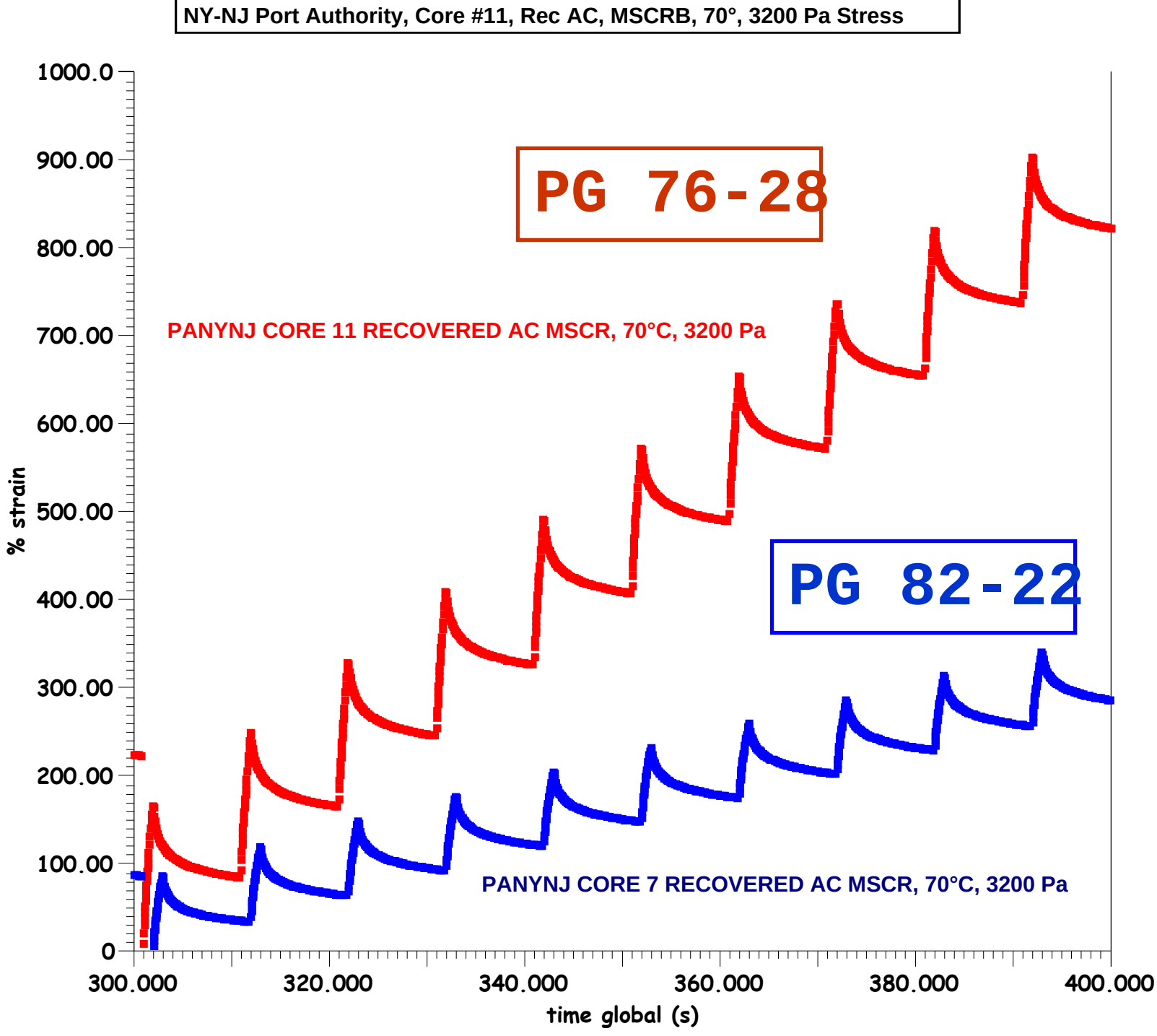
		%P present
64-28	0.211	
58-28	0.324	0.0

APPEARS AS THOUGH TRICHLORETHYLENE ALSO IS REMOVING PHOSPHORUS FROM THE AGGREGATE

FINALLY WE SWITCHED TO TETRAHYDROFURAN (THF)

Sample	%P	Theoretical or actual %P present in binder	Percent phosphorus recovery
Core 7	-0.069	0.0	
Core 13	-0.046	0.0	
Core 11	-0.039	0.0	
58-28 04-28	-0.023	0.0	
acid modified	0.228	0.289	79%


NY-NJ Port Authority, Core #13, Rec AC, MSCRB, 70°, 3200 Pa Stress
PG 64-22
% strain
8000.0
7000.0
6000.0
5000.0
4000.0
3000.0
2000.0
1000.0
0
300.000
320.000
340.000
360.000
380.000
400.000
time global (s)


NY-NJ Port Authority, Core #11, Rec AC, MSCRB, 70°, 3200 Pa Stress
PG 76-28
PANYNJ CORE 11 RECOVERED AC MSCR, 70°C, 3200 Pa
PG 82-22
PANYNJ CORE 7 RECOVERED AC MSCR, 70°C, 3200 Pa
% strain
1000.0
900.00
800.00
700.00
600.00
500.00
400.00
300.00
200.00
100.00
0
300.000
320.000
340.000
360.000
380.000
400.000
time global (s)

PROCEDURE FOR DETERMINING PHOSPHORUS IN BITUMINOUS MIXES

1. Sample of job aggregate needed
   - Determine phosphorus content of aggregate
2. Mix job aggregate with 2 control binders—one with 0% P and one with a know level of P
   - Extract and recovery with Soxhlet using n-propylbromide. This would be preferable to THF
   - If it appears that nPB is removing P from aggregate, switch to THF

PROCEDURE CONTINUED

3. From what we have seen most aggregates do not release their phosphorus to the solvent.
   - Running the control binders will give a good indication of how intensively the aggregate holds on P from PPA or how readily the aggregate gives up its P
4. Run the extraction and recovery of the mix in question

PROCEDURE CONTINUED

5. Soxhlet procedure
   - Use 125-130 grams of mix (should yield ≅ 6+ grams of binder. Sufficient to run XRF test
   - Extract in Soxhlet for 3 hrs
     - We have found that we need to control the extraction time to achieve consistent results between controls and unknowns
6. Recovery procedure for THF using Rotovap
   - Recovery Temp=125°C, Argon gas purge 500 ml/min
   - Start argon purge at 750 mbar (560 mm Hg) ramp down to 200 mbar (150 mm Hg) *below 200 mbar THF boils in receiving flask*
   - Starting rpm=25 ramp to 45 rpm in the 30 minutes at 200 mbar
   - 30 minutes at 200 mbar to be sure all THF removed since the vacuum isn't as low as when we use nPB

SUMMARY & FURTHER WORK

- EDXRF is a suitable and accurate test method for determining percent P typically found in PPA modified asphalt blends.
- Deconvolution of P and S is possible at levels which are typically found in asphalt.
- P in asphalt can be analyzed much faster than with the typical ICP method although with less precision at very low concentrations.

SUMMARY & FURTHER WORK

- Typical extraction solvents (n-Propyl Bromide, Toluene/Ethanol, Tetrahydrofuran) remove differing amounts of phosphorus as a function of the solvent
- Granite, siliceous gravel, and limestone appear to hold on to phosphorus at differing levels after extraction of asphalt—recovery not quantitative
- Some aggregates will release P into extraction solvent

QUESTIONS
COMMENTS