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Overview of Analytical Methods for selected Verdesian Life Sciences Polymer Products

AAPFCO 2016 WINTER ANNUAL MEETING
FEBRUARY 23, 2016

Background on Product Composition and Applicable Analytical Techniques

- PARTIAL SALTS OF CARBOXYLATED COPOLYMERS IN (MOSTLY) AQUEOUS SOLUTIONS

- PRODUCT TEST SEQUENCES
  - public, label claims support methods
  - internal, sequence for manufacturing control

- MOSTLY ASTM METHODS

Product Composition

- **AVAIL® PRODUCTS, AQUEOUS SOLUTIONS**
  - For **liquid** phosphate fertilizers, partial NH_4 salt, about pH 2
  - For **granular** phosphate fertilizers, partial Na salt, about pH 7
    - optionally with propylene glycol

- **NUTRISPHERE-N® PRODUCTS, AQUEOUS SOLUTIONS**
  - For **liquid** nitrogen fertilizers, partial Ca salt, about pH 1.3
  - For **granular** nitrogen fertilizers, partial Ca salt, about pH 2.5
    - with propylene glycol

AVAIL® Phosphorus Fertilizer Enhancer

NutriSphere-N® Nitrogen Fertilizer Manager

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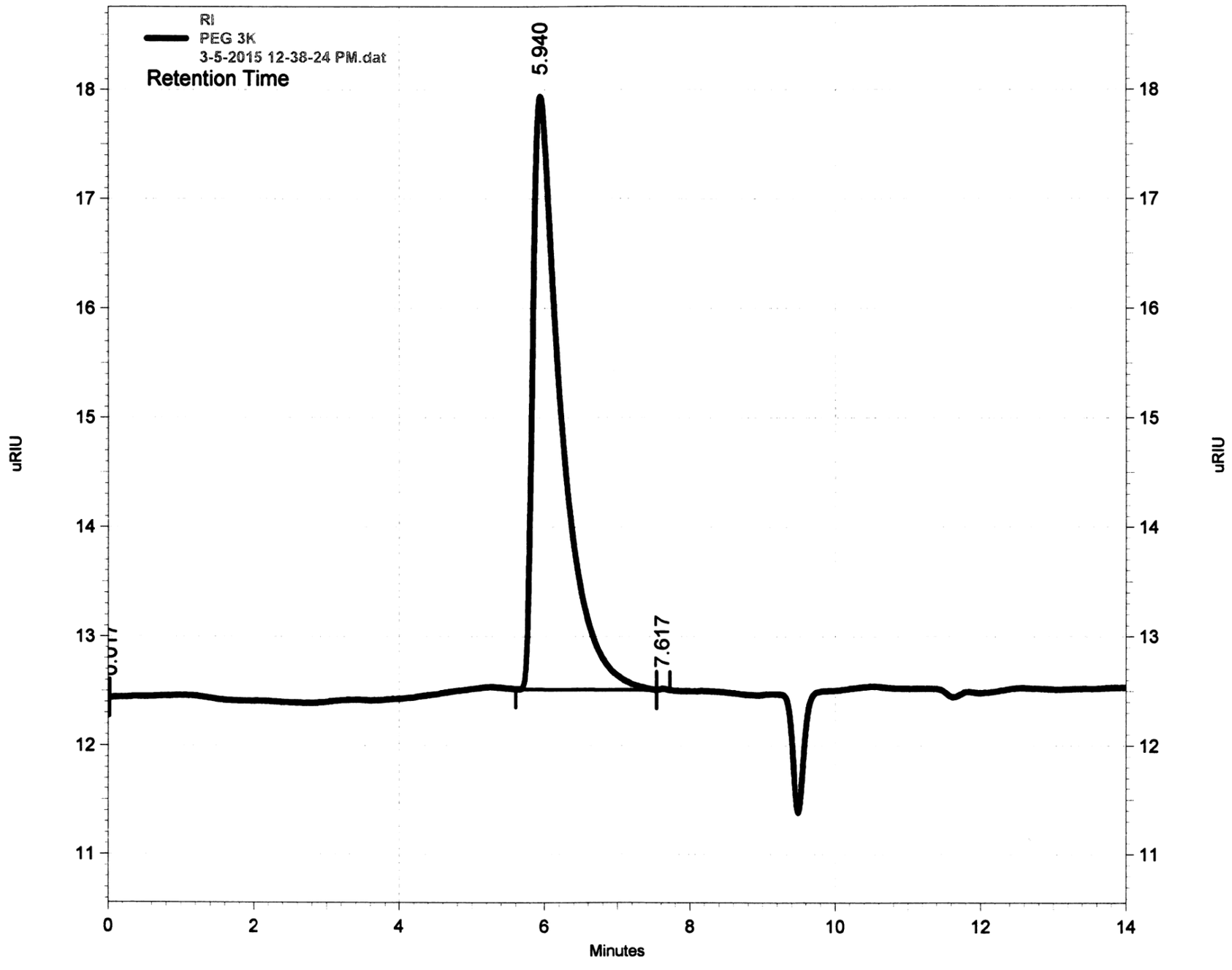
Product Test Sequence

- PUBLIC TO SUPPORT LABEL CLAIMS
  - ASTM METHODS
    - E203-08, volumetric Karl Fischer test for water content in product
    - D4052-11, density test
    - E70-07, pH test
  - OTHER PUBLIC METHODS
    - for confirmation of cation identity (Na, Ca, NH_4)
  - PUBLIC VLSCI CHROMATOGRAPHY METHOD (SIMPLE)
    - quantitative for propylene glycol
    - qualitative for confirming product is polymeric
    - easy, simple, cheap, fast

Typical SEC Single Column Chromatogram

Polymer elution time standard



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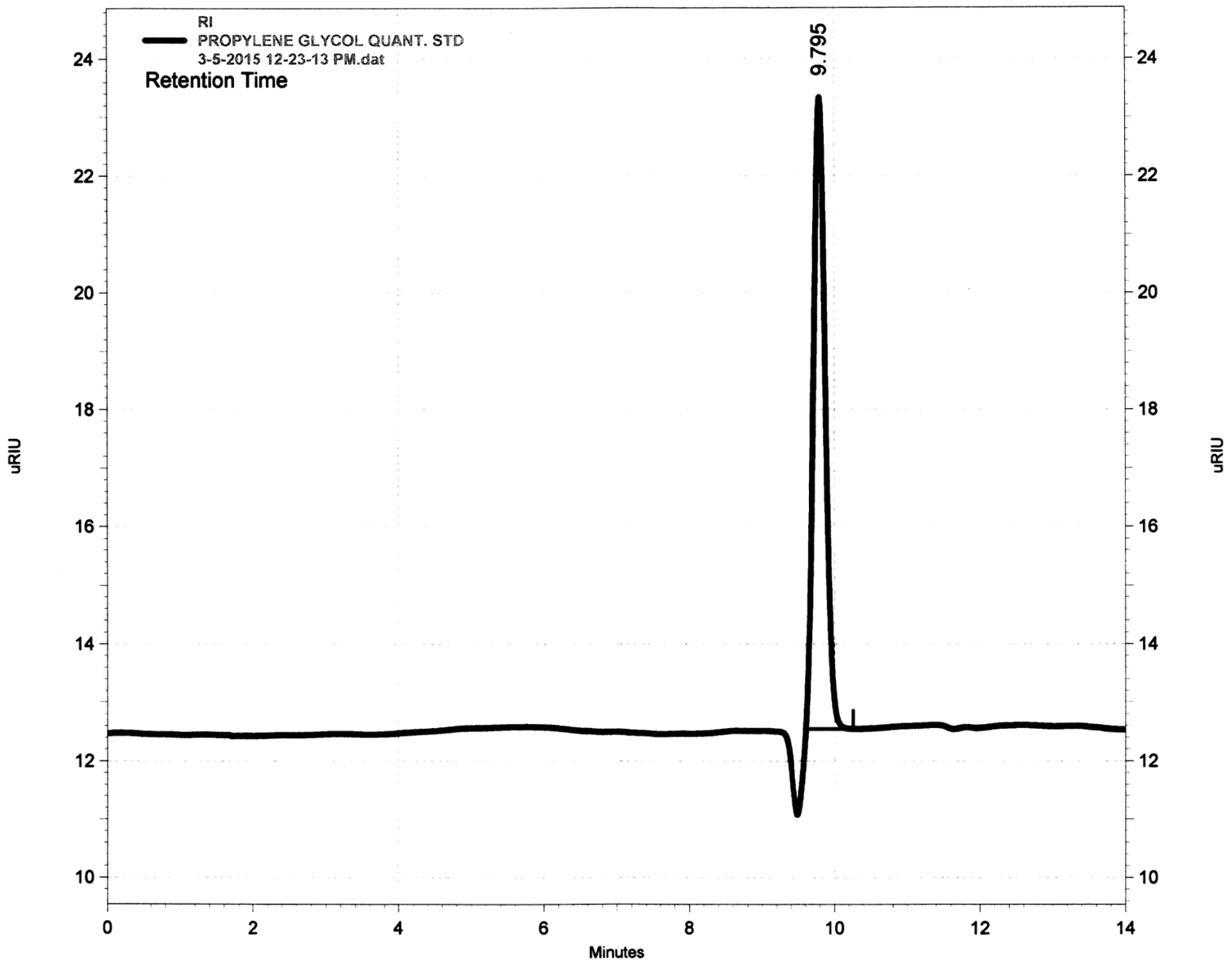
Typical SEC Single Column Chromatogram

Small molecule elution time standard



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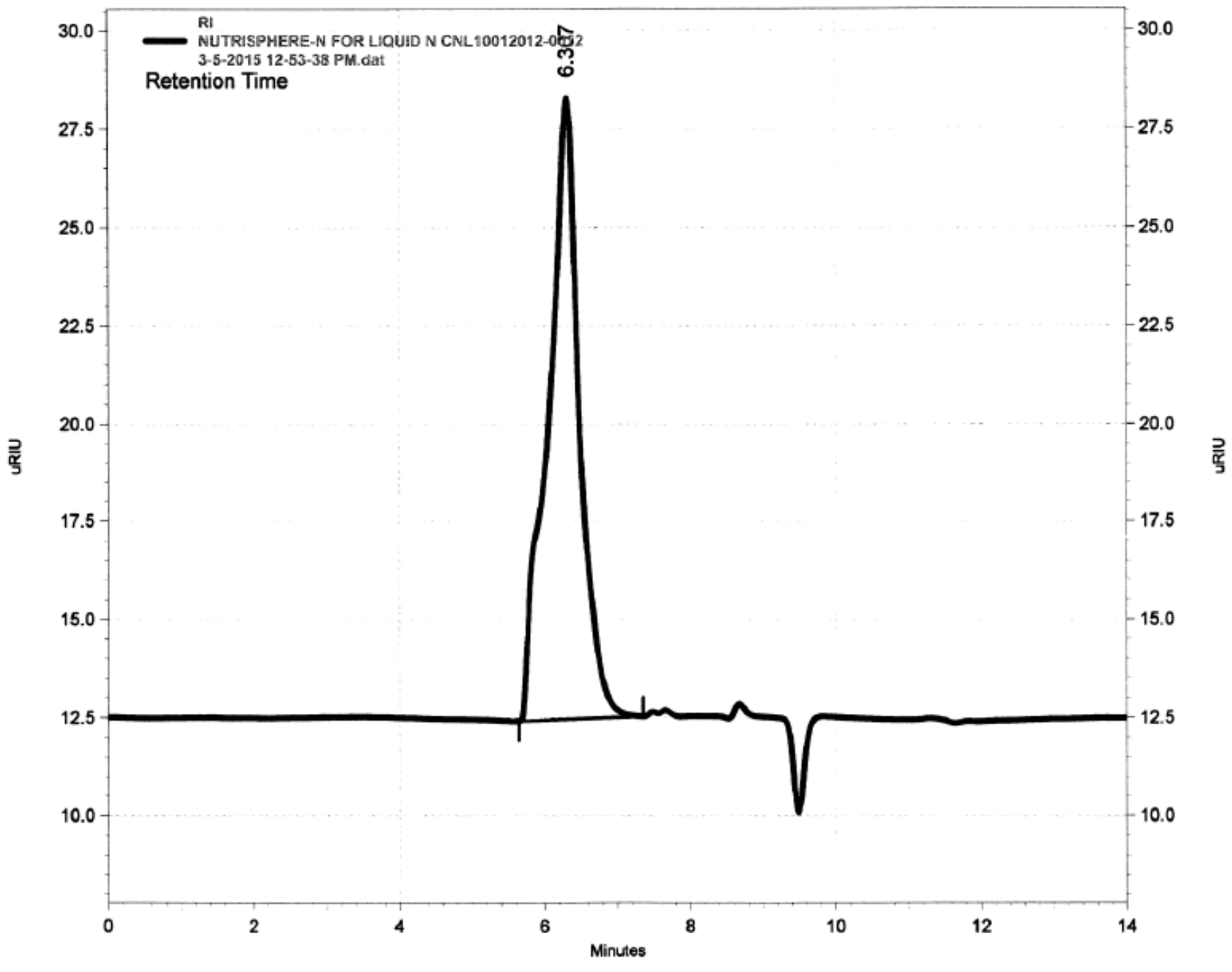
Typical SEC Single Column Chromatogram

Nutrisphere-N for Liquid N Fertilizers



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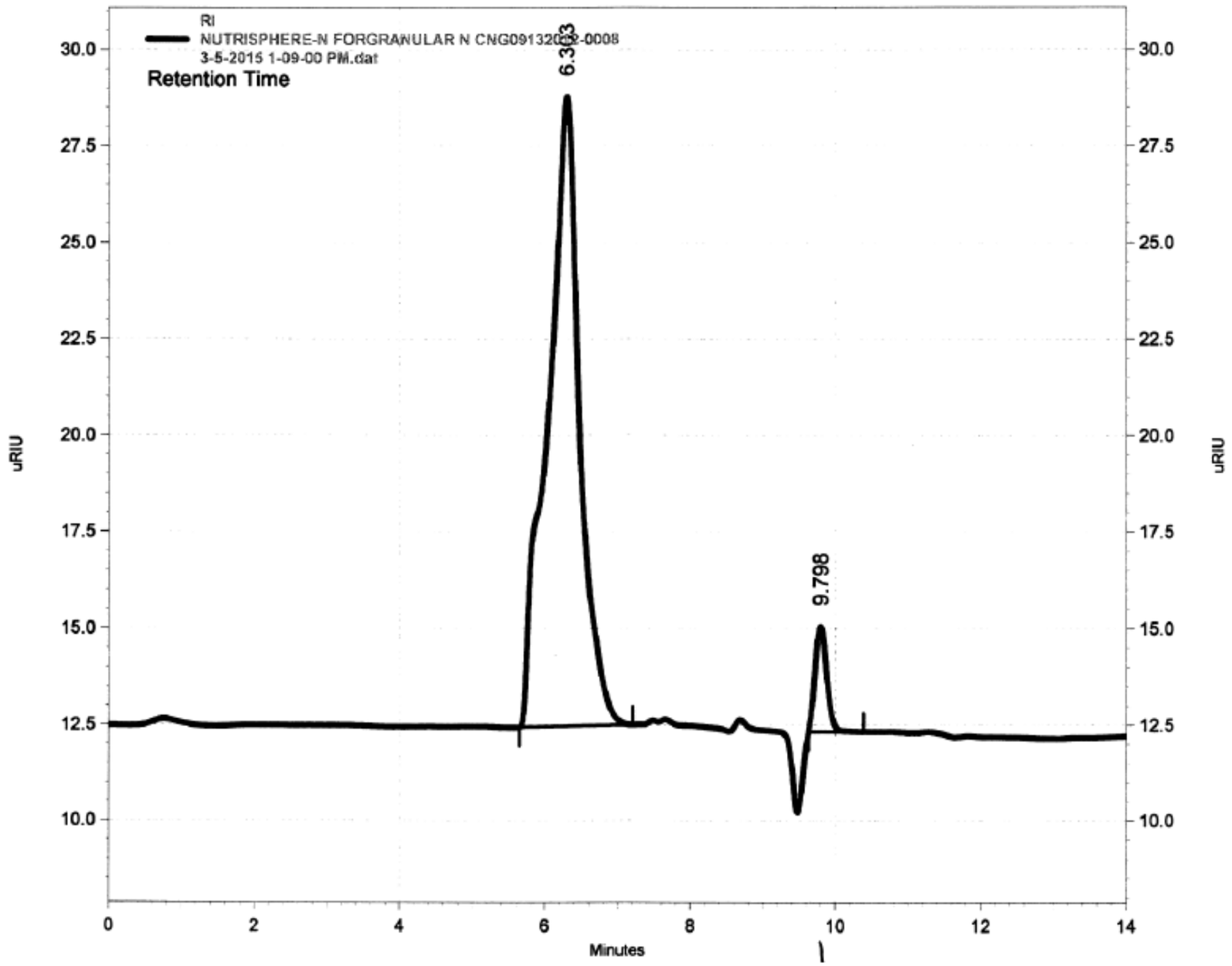
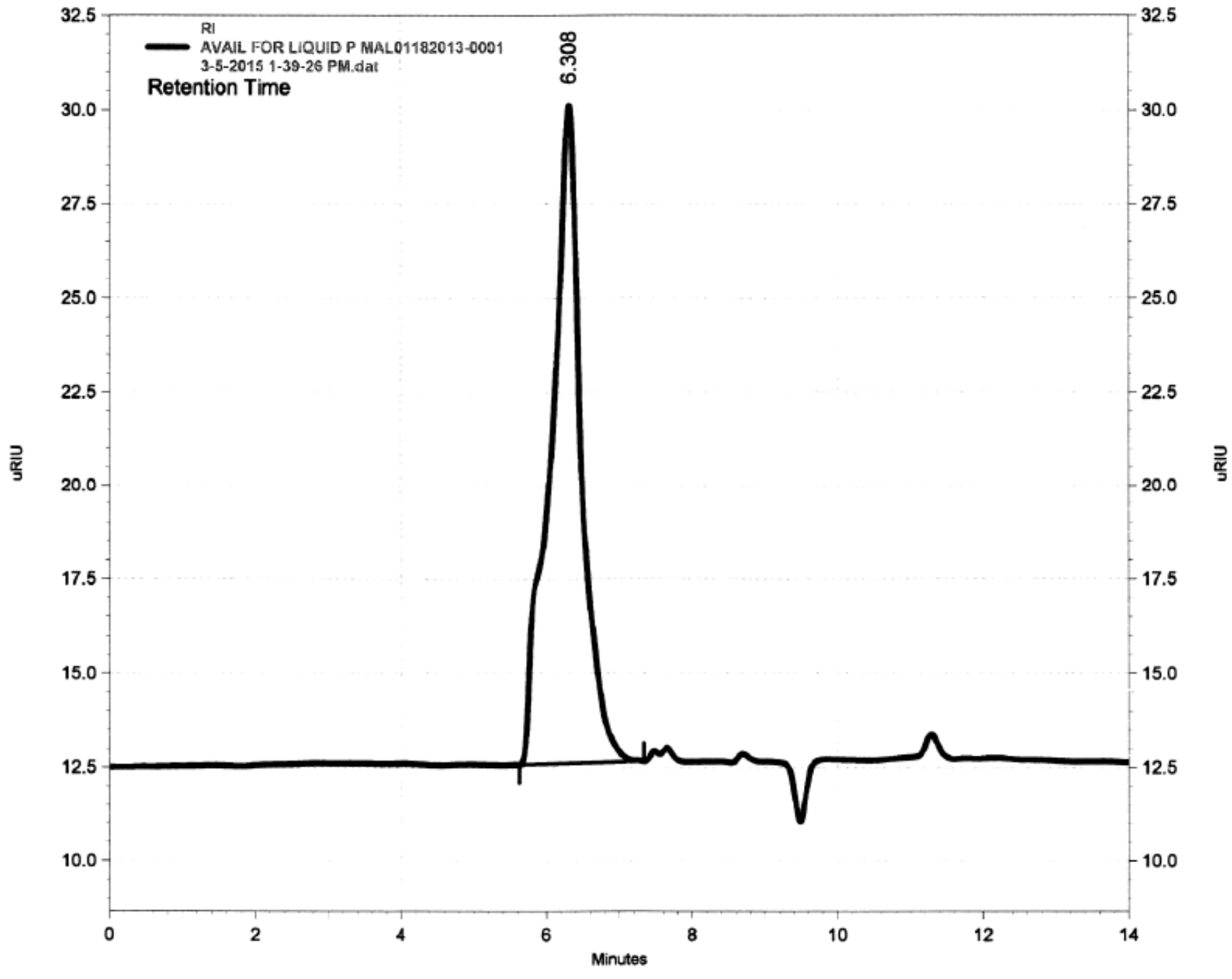
Typical SEC Single Column Chromatogram

Nutrisphere-N for Granular N Fertilizers



Typical SEC Single Column Chromatogram

Avail for Liquid P Fertilizers



Product Test Calculations

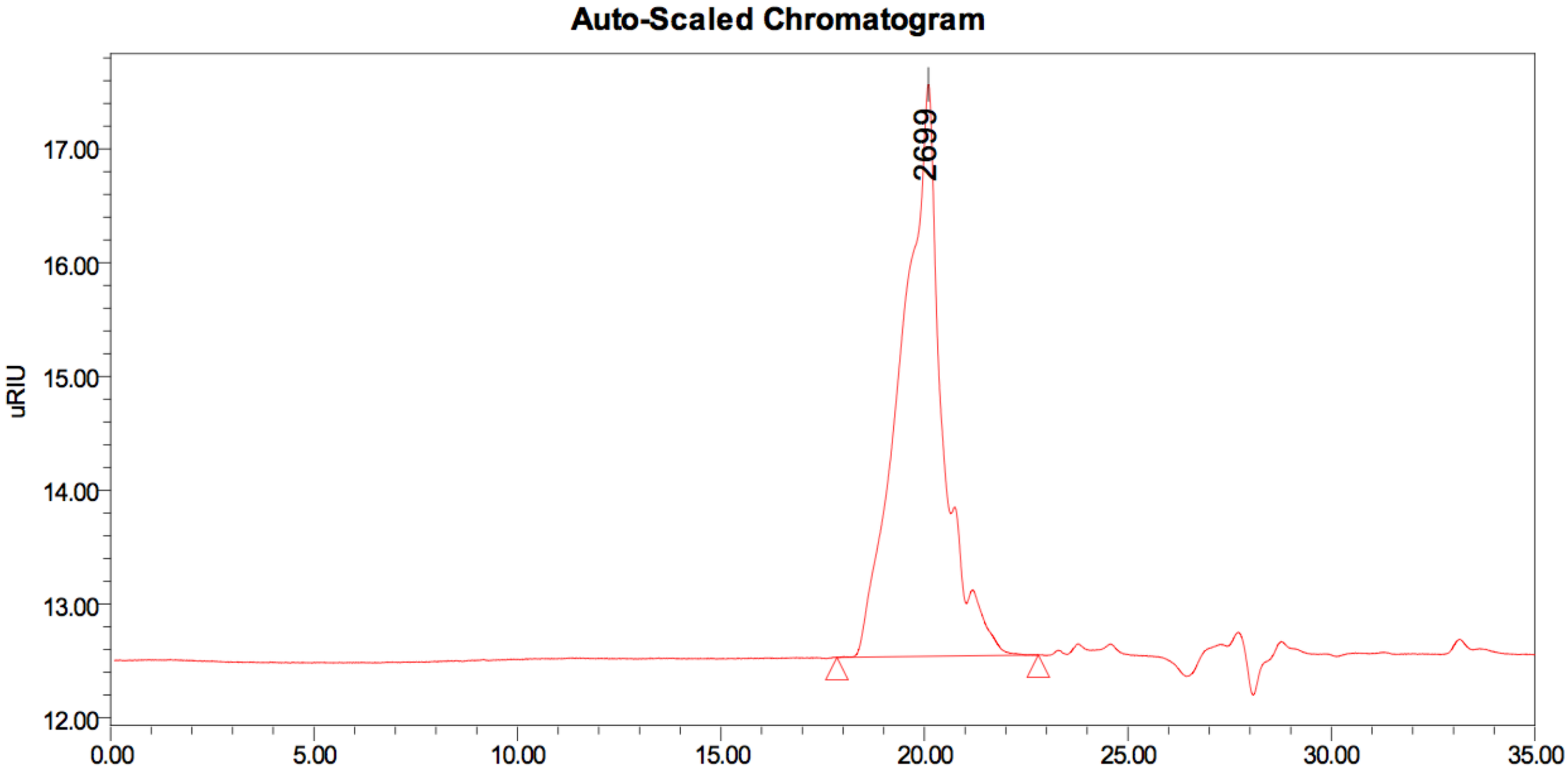
- TO SUPPORT LABEL CLAIMS REGARDING SOLIDS CONTENT
  - Indirect method for polymer due to limitations of chromatography technique
  - Chromatography method demonstrates presence of polymer qualitatively, and (when present) detects and quantitatively determines propylene glycol content
  - Karl Fischer titration quantitatively determines water content
  - Subtract water and propylene glycol content (where present) from 100% to quantitatively determine polymer content

Our Product Test Sequence

- INTERNAL TO SUPPORT PRODUCTION
  - All public sequence ASTM methods, more ISO&ASTM method(s) for internal controls (e.g. dilution detection, etc.)
  - Internal VLSCI chromatography method, just like public method, BUT
    - many more columns, much longer analysis time
    - more detectors, more controls, more analytes, more calibrations
    - numerical calibration of multiple aspects for production control
    - controls production, prevents deviations, detects “drift” in process
    - tough, expensive, complicated, slow, demanding on analyst and equipment

Typical SEC Triple Column Chromatogram

Avail for Liquid P Fertilizers



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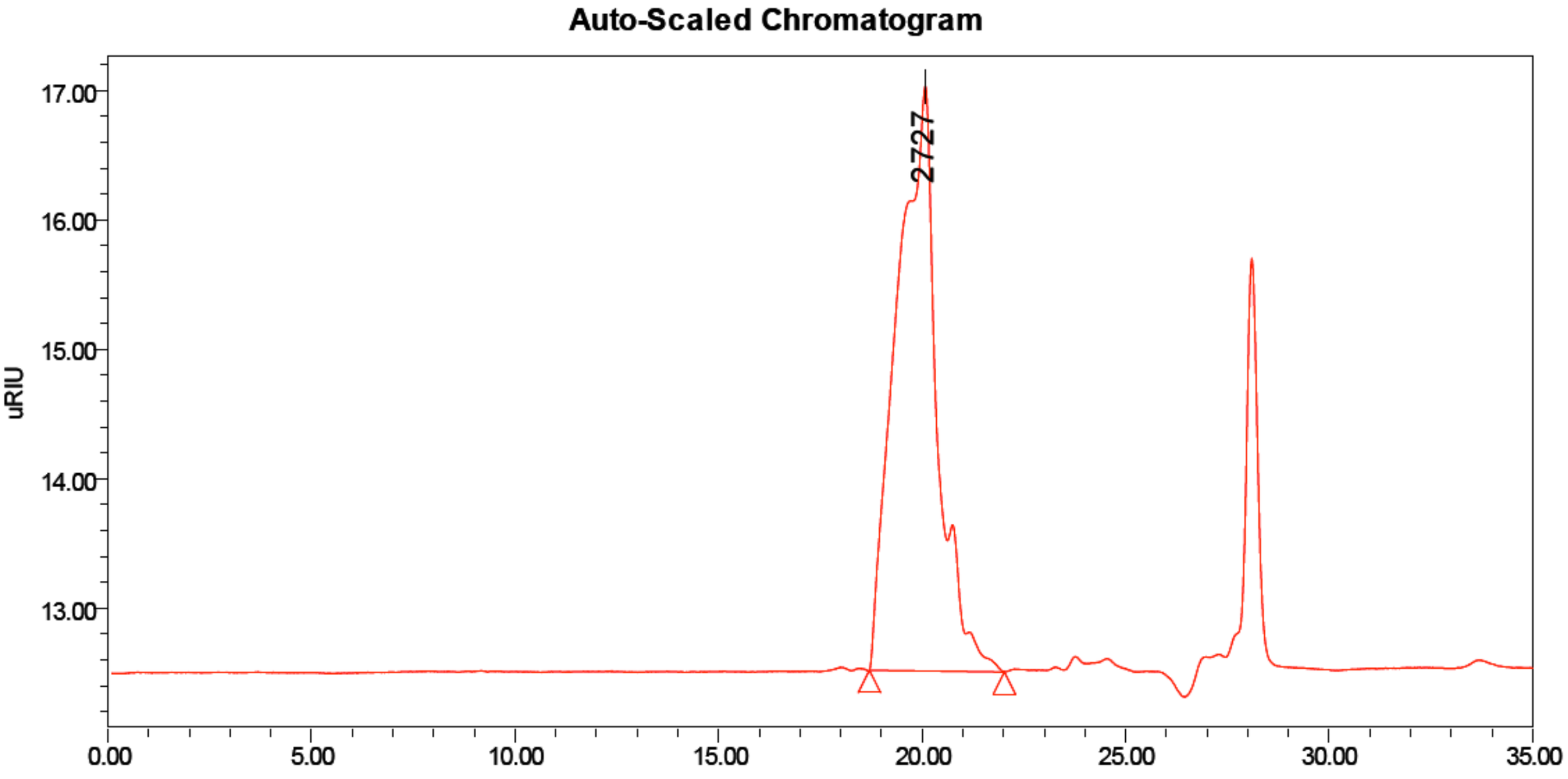
Typical SEC Triple Column Chromatogram

Avail for granular P Fertilizers



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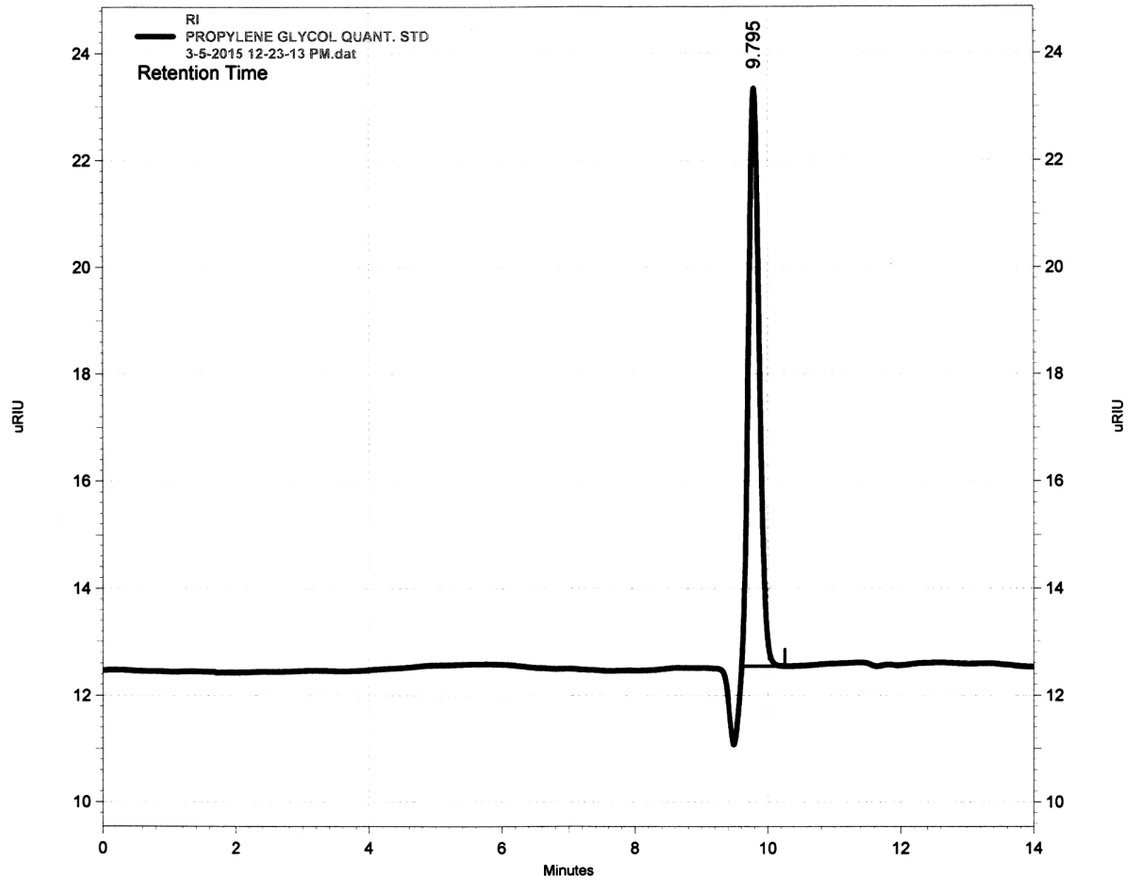
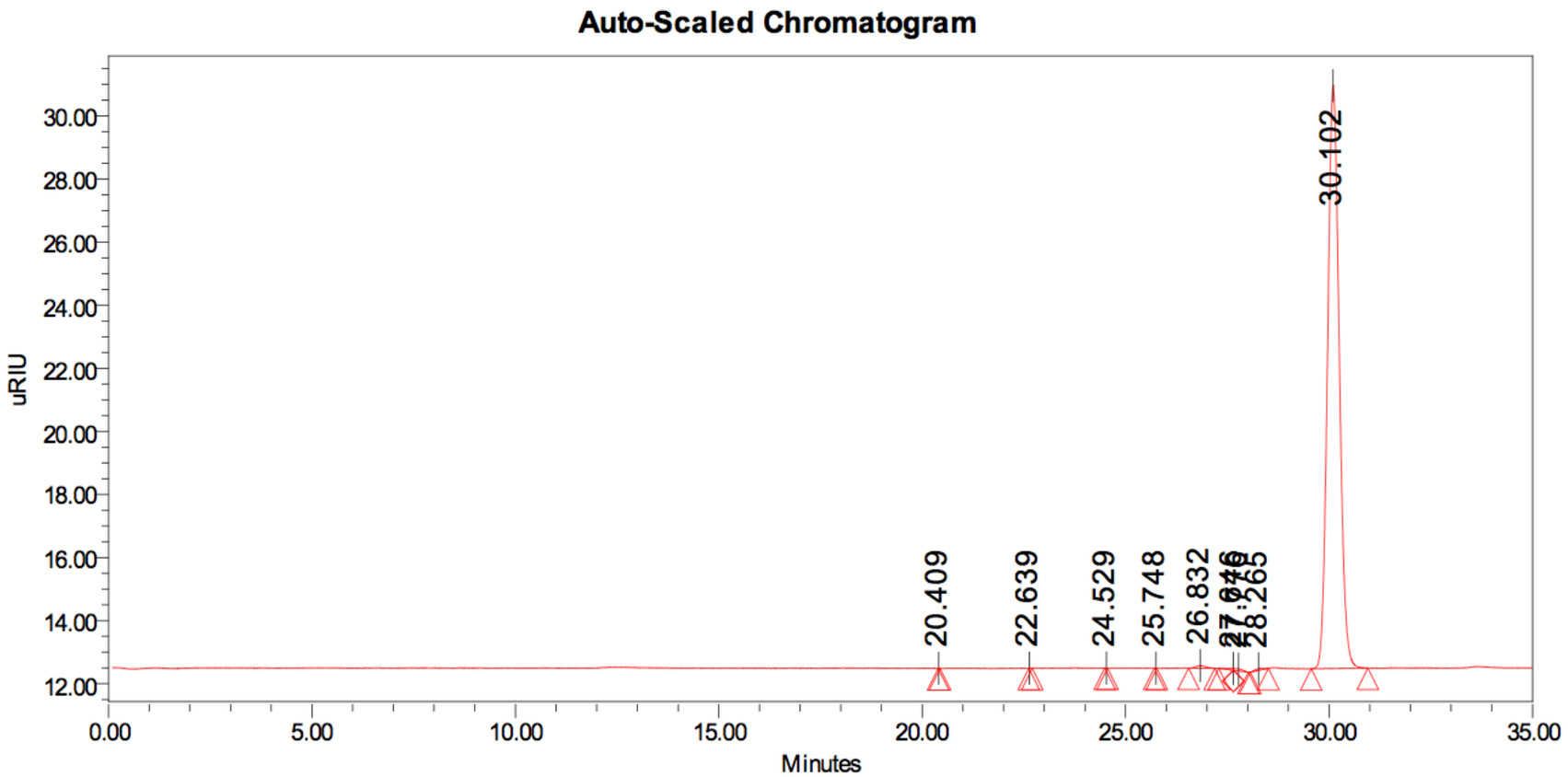
Typical SEC Chromatograms

“Same” results from both methods





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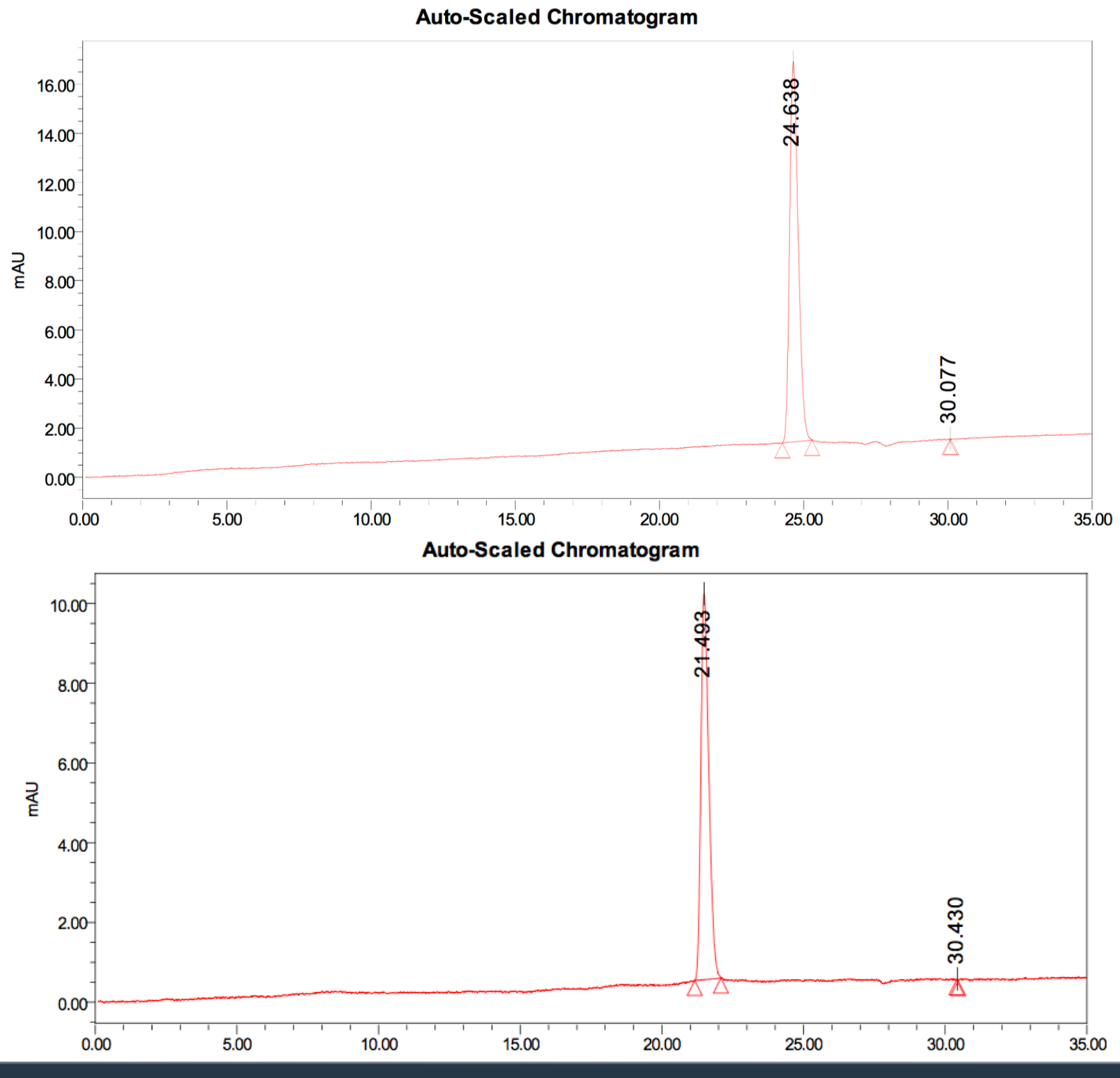
Typical SEC Chromatograms
Additional calibrations from internal method (monomers)



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Public Chromatography Test

- TO SUPPORT LABEL CLAIMS
  - Confirms product is polymeric
    - differentiates between small molecules (monomers, ethylene glycol, propylene glycol) and larger molecules (PEG standard, our polymer analyte with molecular weight similar to PEG standard)
  - Detects (if present) and quantitatively measures propylene glycol content
- WHAT THIS METHOD CANNOT DO FOR EQUIPMENT/WORKLOAD REASONS
  - quantitative in depth molecular weight distribution ANALYSIS
  - trace monomer analysis
- WHAT THIS METHOD CANNOT DO FOR FUNDAMENTAL REASONS
  - quantitative determination of polymer content

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Chromatography Disabilities

- WHY QUANTITATION OF POLYMER LEVELS USING GPC/SEC FAILS
  - Product is a mixture of different molecular weight components
  - Detector response varies with molecular weight and comonomer ratios for lower polymers
  - Batch to batch variation of molecular weight and comonomer ratios sufficient to make quantitation highly inaccurate
  - Result (if tried) is that calibrating with one batch and measuring on another gives wrong result
  - Absolute methods (light scattering) and others (viscometry) work poorly at these molecular weights and with polyanionic species

QUESTIONS

- Thank you!