On-line Detection and Removal of Radioactive Iodine from Aqueous Systems through the use of Scintillating Exchange Resin

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Outline

- Why Radioactive Iodine?
- Iodine Chemistry
- Methods for Iodine Detection
- Scintillating Resins
- Objectives
- Summary Results
- Going Forward

Radioactive Iodine in the Environment

- Two Primary Sources:
  - ^{129}I and ^{131}I are produced as fission products during the production of nuclear power
    - Long half-life of ^{129}I (1.57×10^7 yrs) makes it a persistent contaminant at nuclear waste sites
  - $^{125/131}I$ is commonly used for the treatment of cancer
    - High water solubility (1840 g/L for NaI and 81 g/L for $NaIO_3$) facilitates contamination of the aqueous waste stream and likely passage through waste water treatment

Why Are We Concerned?

- Increased growth of nuclear power industry
  - Increased reactor operation and burn-up
  - Increased radioactive waste generation
  - ^{129}I is a high inventory nuclear waste product as fission product
  - ^{129}I is a long-term risk driver for radioactive waste
  - Necessity for monitoring waste sites for ^{129}I mobility
- Growing concern over clandestine nuclear activities
  - e.g. development of "dirty bombs"
  - ^{131}I readily available from medical field
- Possible contamination of drinking water with $^{125/129/131}I$

http://media.independentmail.com/and/content/img/photos/2008/07/16/OconeeNuke35yrs4_t220.jpg

More Concerns…

- Increased risk associated with exposure to radioactive iodine
  - Propagates through milk pathway
  - Tendency to accumulate in the thyroid
  - Long half-life of ^{129}I and typically low environmental concentrations make detection difficult

http://www.catf.us/projects/power_sector/power_plant_waste/ppw-pathways.jpg

Safe Drinking Water Act (SDWA)

- Sets Maximum Contaminant Level (MCL) for beta-emitters at 4 mrem/yr
  - ^{131}I:
    4.98×10^{-10} µg/L
    ~2.3 Bq/L and ~62 pCi/L
  - ^{129}I:
    0.0613 µg/L
    0.402 Bq/L and ~11 pCi/L
- The DOE regulates to 1 pCi/L

http://www.health-and-wellness-delivered.com/image-files/drinking-water.jpg

Iodine Chemistry

- Iodide (I^-) tends to dominate in anoxic waters
- Iodate (IO_3^-) is the more dominant species in oxygenated waters
- Dissolved organic iodine (DOI) is highly variable depending on organic carbon content
  - Prone to electrophilic aromatic substitution w/ phenolic and α-methyl carbonyl groups
- IO_3^- and DOI (K_d on the order of 1000 cm^3/g) tend to sorb more strongly than I^- ($K_d \leq 1 cm^3/g$)

Environmental Aqueous Iodine

Species		Conc. (µg/L)	System
I^-	Min.	< 1	Coastal surface seawater
	Max.	40	deep ocean and freshwater
IO_3^-	Min.	< 3	estuarine and freshwater
	Max.	60	deep ocean water
DOI	Min.	0.065	ambient SRS groundwater
	Max.	5.7	SRS groundwater + wetland sediment

Standard Iodine Detection Methods

Source	Species	Method	Detection Range (µg/L)
AWWA	I^-	Leuco Crystal Violet	50 – 6,000
	I^-	Catalytic Reduction	<80
	I^-	Voltammetry	0.13 – 10
	IO_3^-	Differential Pulse Polarography	3 -1 30
EPA	I^-/IO_3^-	Method 902.0: Precipitation – Beta Scintillation	None Given

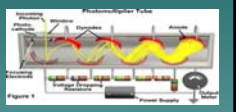
- Most methods are confined to a single matrix (i.e. freshwater, seawater, blood, urine, etc.)
- Sensitive to salts and organics
- Requires multiple steps including precipitation and/or preconcentration methods
- Time-consuming
- Quantification of multiple species requires multiple analyses

Non-Standard Iodine Detection Methods

Species	Method	Detection Range (µg/L)
I^-	HPLC	~0.13
	Capillary Electrophoresis	1.27
IO_3^-	HPLC	~0.13
	ICP-MS	0.00565
	Capillary Electrophoresis	38.13
DOI	HPLC	Indirect

Scintillating Ion Exchange

- Heimbuch, 1962
  - Synthesized plastic phosphor beads by a suspension-type polymerization
  - POPOP scintillator was added to monomer solution
  - Added sulfur-based ion-exchange sorbent to polymer
  - Coupled the resin to a PMT to measure sorbed activities of ^{90}Sr, ^{90}Y, ^{239}Pu, ^{210}Po, and ^{241}Am → Off-line Analysis
  - Detection efficiencies between 40 – 60%
  - No additional scintillation cocktail (improvement over LSC)
  - Flexibility to perform gross activity measurements



http://www.astro.virginia.edu/class/oconnell/astr130/im/photomultiplier.jpg

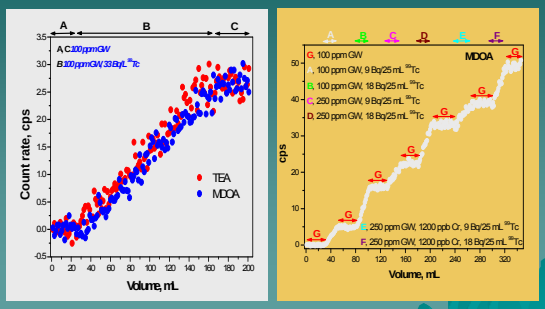
On-line Radiochromatography

- Couple flow-cell scintillation detection with liquid chromatography
- DeVol et al., 2000
  - Used acrylic and styrenic polymer beads infused with PPO and DM-POPOP fluors
  - Utilized ABEC, Aliquat-336, and TEVA extractants (Extraction Chromatography)
  - Detection of ^{99}Tc down to 168 pCi/L (6.2 Bq/L)

On-line Measurements

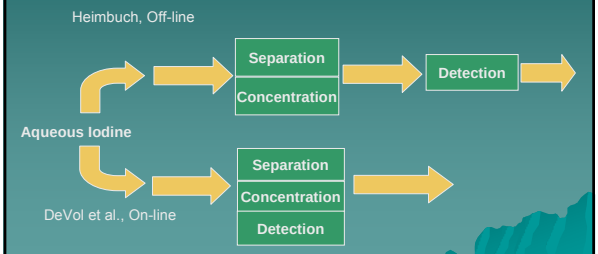
- Advantages
  - Sequential elution allows near real-time activity determination
  - Simultaneous separation, concentration, and detection with flow-cell technology
  - Absolute detection efficiencies up to 95% depending on resin and analyte
- Drawback
  - Leaching of extractant/ scintillator over time

On-Line Measurements



Figures Taken from Seliman, 2009

Single-Step Process



Incorporation of Scintillation and Anion Exchange

- Principle
  - Aqueous radioactive iodate is preferentially removed by modified resin
  - Incorporation of organic fluor into resin
  - Promotes higher probability of interaction relative to heterogenous resins
  - Increased detection efficiency
  - Off-line or On-line measurements
- Components
  - Inert polymeric support material
  - Inert organic fluor diffused into polymer
  - Infused liquid anion exchange group

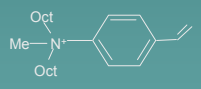
Objectives

1. Identify an anion exchange group selective for iodate
2. Synthesize homogeneous scintillating exchange resin
3. Utilize resin in an on-line flow-cell scintillation detection system
4. Characterize resin in terms of capacity, kinetics, on-line loading efficiency, detection efficiency, and interferences

http://cache3.asset-cache.net/xc/200277984-001.jpg?v=1&c=NewsMaker&k=2&d=F60B35220888707 72E6A8A3FFE90EB24D4B40B3E875A785D

1. Anion Exchange Group

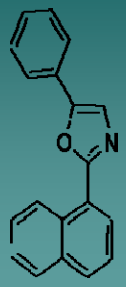
- Previous studies by Seliman et al. (2010) identified N-methyldi-n-octylamine (MDOA) and triethylamine (TEA) as efficient exchange groups for pertechnetate (TcO_4^-)
- Preliminary tests showed MDOA was an effective group for iodate removal



MDOA

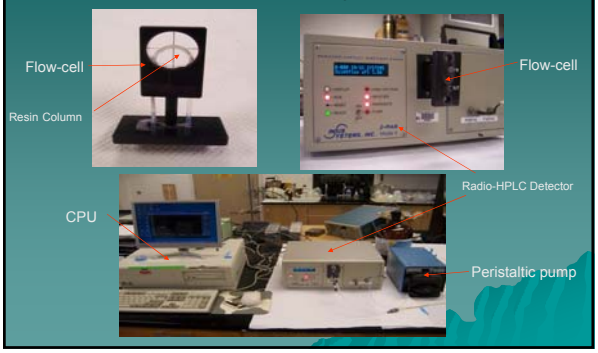
2. Scintillating Exchange Resin Fabrication

- Utilized chloromethyl polystyrene resin as a polymeric support
- Infused resin with 2-(1-naphthyl)-5-phenyloxazole (α-NPO) scintillator
- Aminated resin with MDOA

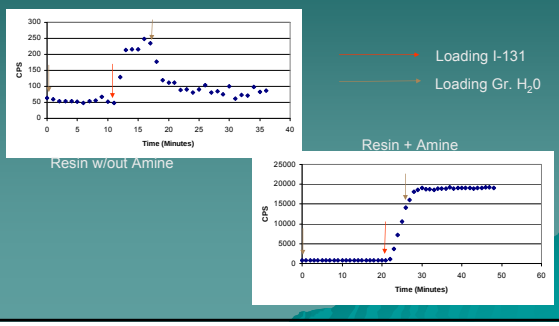


α-NPO

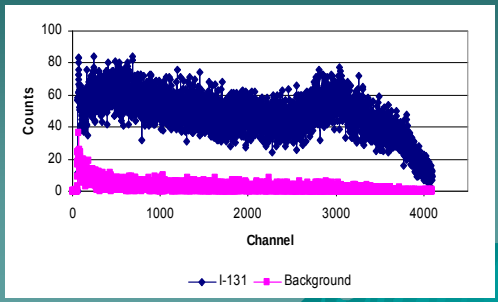
3. On-line Flow-cell Scintillation Detection System



Multi-Channel Spectra



Pulse Height Spectra



4. Resin Characterization

- Run batch and on-line flow-cell experiments to characterize resin:
- Analyses
  - Loading efficiency
  - Detection efficiency
  - Capacity
  - Kinetics
  - Interferences

Summary Results

- Typical Loading ε: ~90%
- Typical Detection ε: ~50%
- Typical Uptake Kinetics: < 2 min
- Capacity: >7.5 meq IO_3^-/g
- MDC: 0.4 Bq/L
  - Volume: 195 mL
  - Count Time: 3.25 hr
- Interferences: NO_3^- and SO_4^{-2} at 50-100x ambient levels

Moving Forward

- Tasks
  - Identification of iodine-selective ligand
  - Resin characterization (capacity, kinetics, pore volume, surface area, packed bed density, interferences, etc.)
  - Flow-cell optimization experiments
  - Collection and analysis of aqueous environmental samples

Acknowledgements

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