Validation of Extraction Chromatography Resin Material Identity Using Fourier Transform Infrared Spectroscopy (FTIR)

Madeleine A. Eddy, Jose Muñoz, and Daniel R. McAlister
Eichrom Technologies, LLC Lisle, IL USA

eichrom TECHNOLOGIES
A GCI COMPANY
1955 University Lane • Lisle, IL 60532 USA
www.eichrom.com

Abstract

Eichrom Technologies manufactures extraction chromatography resins for use in a range of applications, including nuclear medicine. These resins are used to purify radionuclides from target material and other contaminants prior to radiolabeling. Eichrom conducts resin-specific quality control designed to confirm the material identity and performance specifications for each product. However, the final resin materials are nearly identical to each other visually, and customer interest was expressed for a simple, non-destructive identity test as an additional check for all end-users. Herein, the use of Fourier Transform Infrared Spectroscopy (FTIR) to characterize Eichrom's extraction chromatography resins is presented as an option for identity validation of the materials. This simple technique can provide confirmation and distinguish between most Eichrom resins or classes of resins that use similar or identical extractants. Further work to improve the quality of the spectral library is ongoing, with hopes to improve the differentiation between SR/PB, RE/TRU, and DGA-N/DGA-B/DOODA resins.

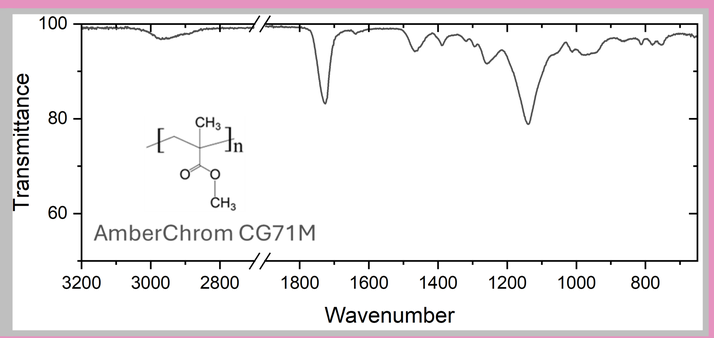
Motivation / Background

- Extraction chromatography resins are typically odorless white powders
  - Hard to distinguish different resins based on physical appearance
  - In-house resin QC employs radiochemical separations
- Nuclear medicine customers may require validation of resin ID on receipt of material
- A simple, non-destructive method for confirming the EXC material is the correct formulation is needed
- **Recently acquired a CARY 630 FTIR instrument with ATR cell**

Eichrom EXC Resins

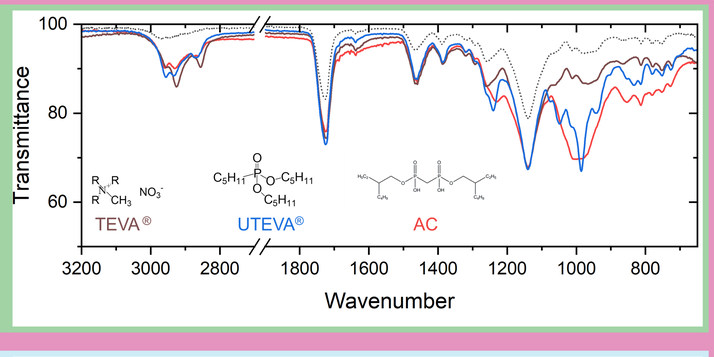
Standard Formulation

- AmberChrom CG71M solid support
- 40% wt. liquid extractant or solid extractant + diluent
  - Physiosorbed to support



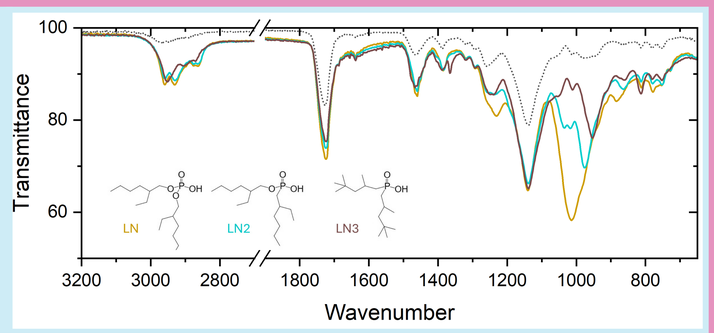
Resins for Actinides

- TEVA: +4 actinides
- UTEVA: +4 actinides and uranium (UO_2^{2+})
- AC: high efficiency gross actinide extraction



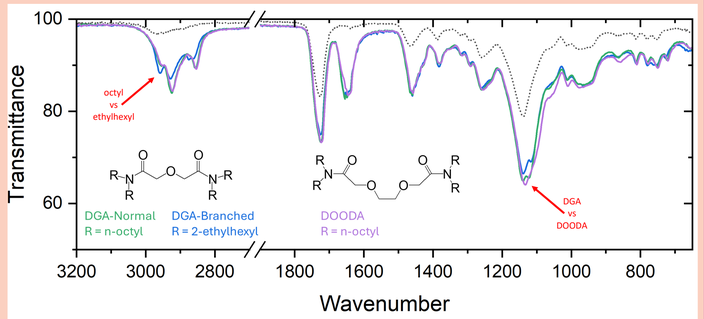
LN Series

- LN, LN2, LN3: similar chemistry
- Acidic organophosphorus extractants
- High SF for adjacent LN's
- Extracts from dilute acid



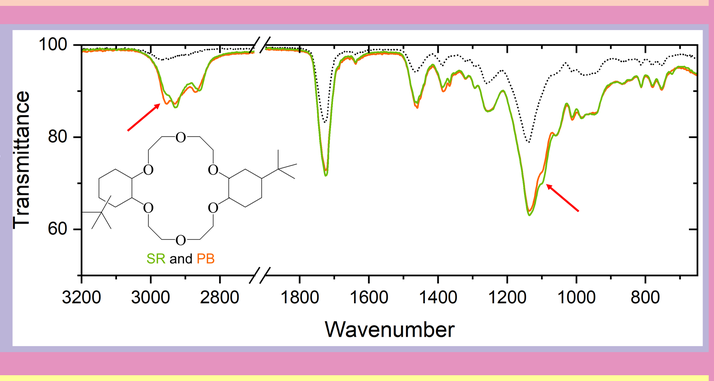
DGA Family

- DGA-Normal, DGA-Branched, DOODA
- All C8-amides with ethylene linkers
- Extracts 3+ and 4+ actinides/ lanthanides from acidic media



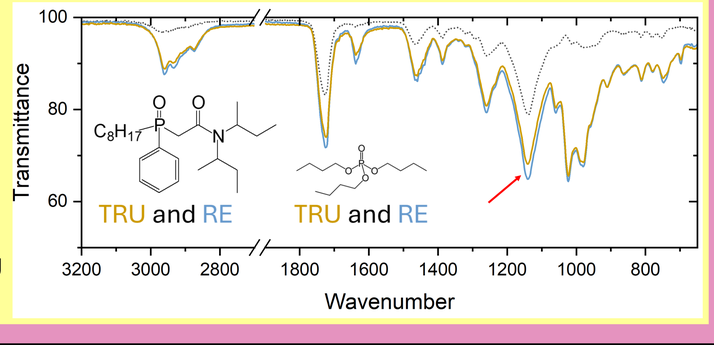
Crown Ether Resins

- Selective for Sr and Pb
- Requires alcohol diluent to fully dissolve crown ether
  - SR = octanol
  - PB = isodecanol



Resins for f-Elements

- TRU: transuranic actinides
- RE: same extractant + diluent as TRU, in different ratios
- RE shows improved uptake of +3 f-elements compared to TRU



ATR-FTIR Spectroscopy

- FTIR spectra of resins represent the chemical features of the extractant, diluent (if present), and solid support
- Peak positions correspond to functional groups

Functional Group		Absorption (cm^{-1})	Intensity
Alkane	C—H	2850–2960	Medium
Alkene	=C—H	3020–3100	Medium
	C=C	1640–1680	Medium
Alkyne	≡C—H	3300	Strong
	C≡C	2100–2260	Medium
Alkyl halide	C—Cl	600–800	Strong
	C—Br	500–600	Strong
Alcohol	O—H	3400–3650	Strong, broad
	C—O	1050–1150	Strong
Arene	C—H	3030	Weak
Aromatic ring		1660–2000	Weak
		1450–1600	Medium

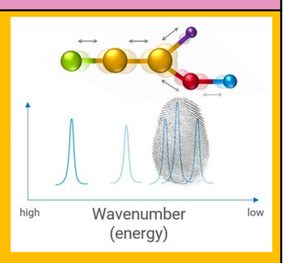
Functional Group		Absorption (cm^{-1})	Intensity
Carbonyl compound	C=O	1670–1780	Strong
	Aldehyde	1730	Strong
	Ketone	1715	Strong
	Ester	1735	Strong
	Amide	1690	Strong
	Carboxylic acid	1710	Strong
Carboxylic acid	O—H	2500–3100	Strong, broad
Nitrile	C≡N	2210–2260	Medium
Nitro	NO_2	1540	Strong, broad
Amine	N—H	3300–3500	Medium
	C—N	1030–1230	Medium

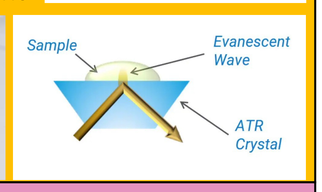
Identity Testing Methods

- Create an Eichrom library with extractants, resins, diluents, and solid supports
- Create a method to match-fit unknown samples using the Eichrom library
- Prepare unknown samples containing Eichrom resins or misc. resins not in Eichrom Library
- Recruit QC chemist (JAM) to measure the unknown samples and use match-fits from the Eichrom library to determine the correct resin ID

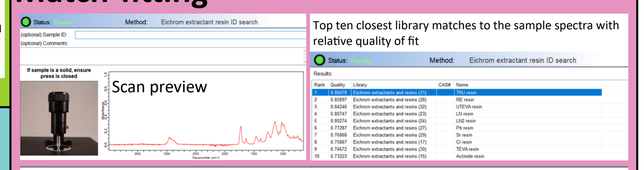
Cary 630 FTIR

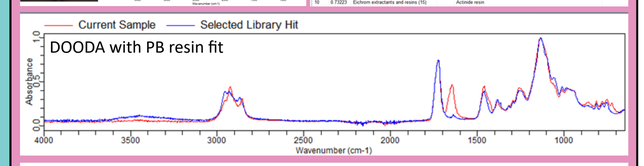
- Portable (3.5 kg)
- Agilent MicroLab software
- < 2 cm^{-1} resolution
- Diamond ATR attachment

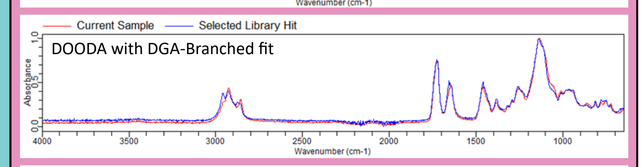


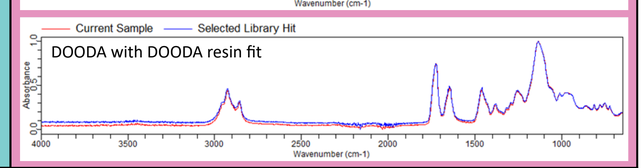


Match-fitting









Results

Sample	Resin	Resin Fit	First Fit	Second Fit	Third Fit	JAM Resin ID
C	**Amberchrom**	0.92292	**Amberchrom**	TEVA	ZR	**Amberchrom**
F	**TEVA**	0.87270	**TEVA**	WBEC	CL	**TEVA**
M	**UTEVA**	0.88755	**UTEVA**	RE	TRU	**UTEVA**
K	**AC**	0.90213	UTEVA	LN	LN2	**AC**
O	**LN**	0.94367	**LN**	TRU	UTEVA	**LN**
B	**LN2**	0.93417	**LN2**	UTEVA	RE	**LN2**
V	**LN3**	0.90316	**LN3**	TEVA	CL	**LN3**
R	**DGA-N**	0.85212	DOODA	**DGA-N**	TEVA	**DGA-N**
A	**DGA-B**	0.84132	DGA-N	DOODA	**DGA-B**	**DGA-B**
G	**DOODA**	0.85303	**DOODA**	DGA-N	DGA-B	**DOODA**
D	**SR**	0.88180	PB	**SR**	TEVA	**SR**
U	**PB**	0.89244	**PB**	SR	TEVA	**PB**
J	**TRU**	0.87032	**TRU**	RE	UTEVA	**TRU**
H	**RE**	0.85859	TRU	**RE**	UTEVA	**RE**

Conclusions

- ATR-FTIR can determine the identity of most extraction chromatography resins
- Spectra are a combination of signatures from the amberchrom support, organic extractant, and diluent (if included) so similar resins have similar spectra
  - *Some difficulty distinguishing between DGA resin family*
  - *Some difficulty distinguishing between SR and PB resin*
  - *Some difficulty distinguishing between TRU and RE resin*
- In instances where the software incorrectly matched the resin, the user compared spectral fits manually and was able to correctly assign the resin ID
- **This basic test case suggests that this technique could be used by nuclear medicine customers as a form of identity testing to confirm resin ID on receipt of materials, though some work to improve the fitting parameters may be required.**

References

McMurry, John E. Organic Chemistry: A Tenth Edition - OpenStax adaptation 1. OpenStax, 2023.

"What is FTIR Spectroscopy? Principles Overview." Agilent Technologies, www.agilent.com/en/support/molecular-spectroscopy/ftir-spectroscopy/ftir-spectroscopy-basics-faqs.