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Validation of EPA Method 524.3 for Low Level Analysis of TCP, EDB, and DBCP

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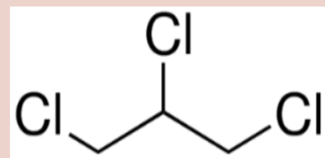
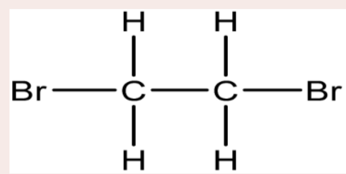
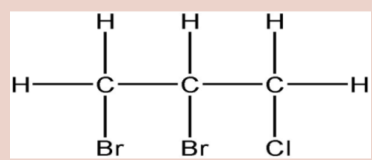
Analytes of Interest

Name	Structure	FW	BP (ºC)
1,2,3-Trichloropropane (TCP)		147.4	157
Ethylene dibromide (EDB)		187.9	132
1,2-Dibromo-3-chloropropane (DBCP)		236.3	196

Analytes of Interest



Name	Health Issues	Sources
TCP	Increased risk of cancer.	Runoff from soil fumigants, industrial/hazardous waste sites, a cleaning/ degreasing agent.
EDB	Increased risk of cancer. Problems with reproductive system, liver, stomach, or kidneys.	Discharge from petroleum refineries.
DBCP	Increased risk of cancer. Problems with reproductive system.	Runoff from soil fumigants.

Current Drinking Water Regulations

Authority	Reg.	TCP	EDB	DBCP
EPA	MCL (ng/L)	---	50	200
	PHG (ng/L)	---	0	0
NJ	MCL (ng/L)	30 (09/04/2018)	50	200
CA	MCL (ng/L)	5.0 (12/14/2017)	50	200
	DLR (ng/L)	5.0	20	10
	PHG (ng/L)	0.7 (2009)	10 (2003)	1.7 (1999)

MCL = Maximum Contaminant Level PHG = Public Health Goal
DLR = Detection limit for purposes of reporting

Reference Methods and MDLs (ng/L)



Compound	Technique	TCP	EDB	DBCP
EPA 502.2 Rev. 2.1, 1995	PT GC/PI-ELCD	10	---	---
EPA 504.1 Rev. 1.1, 1995	LLE GC/ECD	20	10	10
EPA 551.1 Rev. 1.0, 1995	LLE GC/ECD	8	8	9
EPA 524.2 Rev. 4.1, 1995	PT GC/MS (FS)	30	50	20
EPA 524.3 Rev. 1.0, 2009	PT GC/MS (FS)	50	18	63
	PT GC/MS (SIM)	---	1.0	1.6
SRL 524M-TCP 2002	PT GC/MS (SIM)	---	---	---

CA State Water Quality Control Board: 2018 (Q1, Q2, Q3)
569 sources within 30 counties exceeded TCP MCL.



Quarter
All

Drinking Water Source Status
All

Reset to Default

Drinking Water Sources
569

5-10 ppt	225
10-15 ppt	121
15-20 ppt	87
> 20 ppt	293

County	Drinking Water Sources
BUTTE	3
DEL NORTE	1
FRESNO	108
KERN	147
LAKE	1
LOS ANGELES	36
MADERA	9
MARIPOSA	1
MENDOCINO	1
MERCED	44
MONO	1
MONTEREY	8
NAPA	1
RIVERSIDE	18
SACRAMENTO	4
SAN BERNARDINO	16
SAN DIEGO	8
SAN JOAQUIN	36
SAN LUIS OBISPO	1
SAN MATEO	3
SANTA CLARA	2
SANTA CRUZ	4
SONOMA	1
STANISLAUS	50
SUTTER	1
TULARE	57
TUOLUMNE	1
VENTURA	2
YOLO	1
YUBA	3
Total	569

57 Labs Currently Certified in NJ for TCP, EDB, and/or DBCP



Methods	No. of Labs
EPA 502.2, Rev. 2.1, 1995	1
EPA 504.1, Rev. 1.1, 1995	14
EPA 524.2, Rev. 4.1, 1995	37
EPA 524.3, Rev. 1.0, 2009	5

Method Validation



	EPA 504.1	SRL 524M-TCP	EPA 524.3
Container	40 mL glass VOA vials	40 mL amber glass VOA vials	40 mL amber glass VOA vials
Preservative	6 mg sodium thiosulfate	25 mg ascorbic acid	25 mg ascorbic acid 200 mg maleic acid
Preparation	35 mL sample 2 mL hexane	25 mL purge vessel	5 mL purge vessel

Method Validation

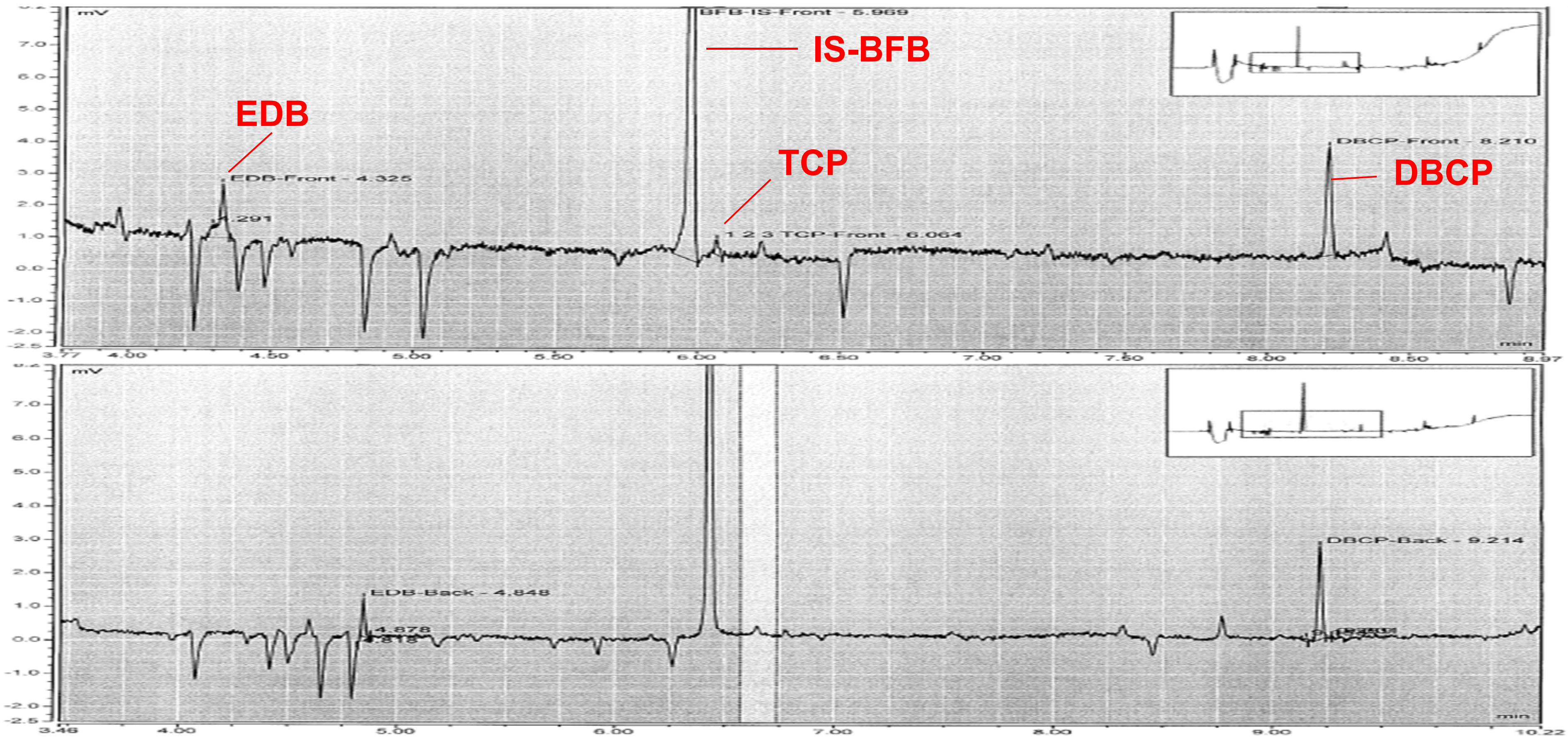
- **EPA 504.1**

  - Varian CP-3800 GC
  - LLE procedural calibration
  - Internal standard quantitation

- **EPA 524.3 and SRL 524M-TCP**
  - Agilent 7890B GC/5977A MSD, Teledyne Tekmar Stratum P&T Concentrator, and AQUATek 100 Autosampler

  - P&T procedural calibration
  - Internal standard quantitation

504.1 TCP, EDB & DBCP at 30 ng/L
IS-Bromofluorobezene (BFB) at 100 µg/L



EPA 504.1: Accuracy and Precision

Spiking Conc. = 100 ng/L



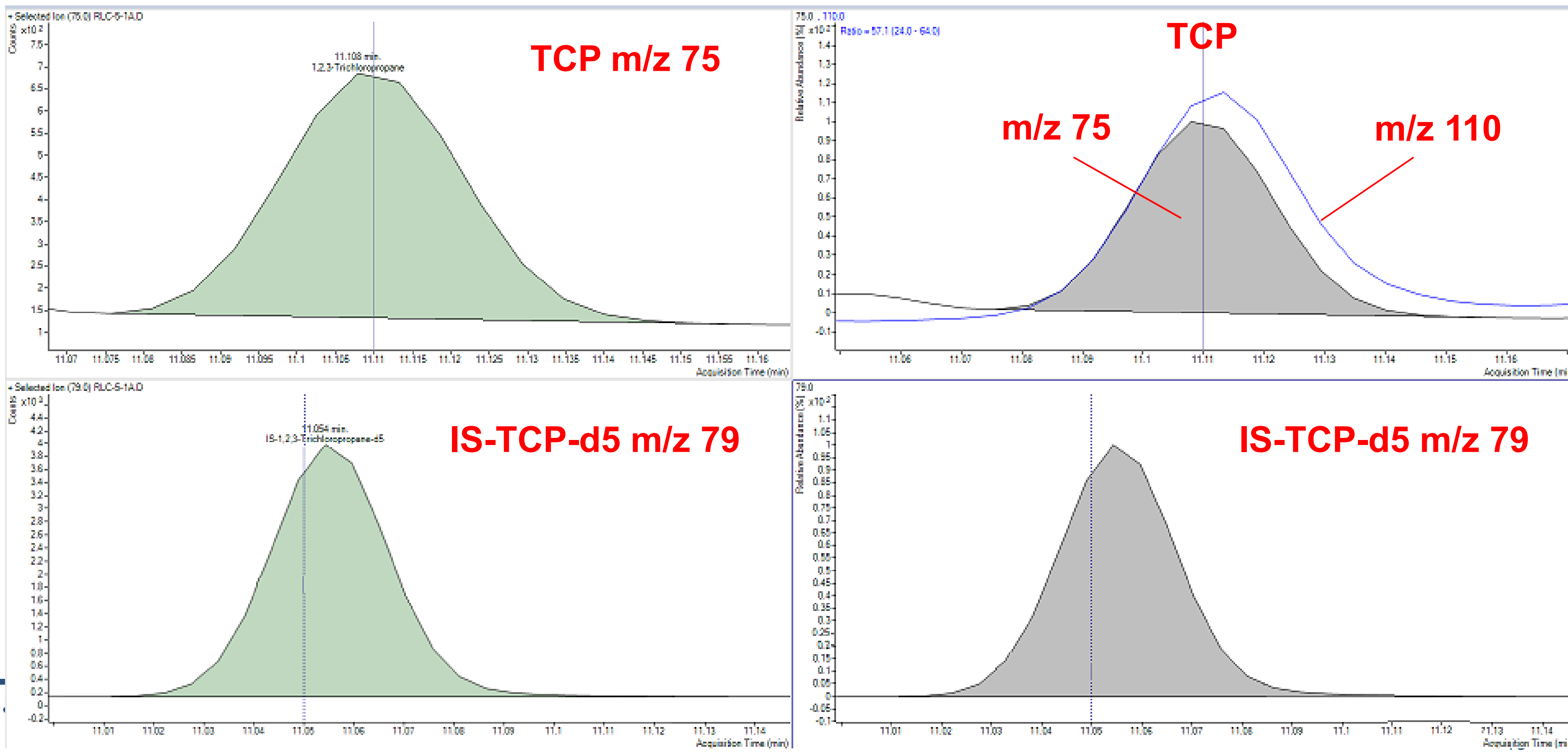
Analyte	Column/Det.	Recovery (n=4) (%)	RSD (n=4) (%)
TCP	Front	96	5.6
	Back	99	7.5
EDB	Front	91	5.8
	Back	111	4.9
DBCP	Front	105	2.3
	Back	107	1.7

EPA 504.1: Sensitivity (n = 7)

Analyte	Spiking Conc. (ng/L)	Column/Det.	MDL (ng/L)
TCP	30	Front	12.1
		Back	13.1
EDB	10	Front	4.2
		Back	6.2
DBCP	10	Front	5.1
		Back	5.8

SRL 524M-TCP at 5 ng/L
IS-TCP-d5 at 0.2 µg/L





SRL 524M-TCP: Accuracy and Precision

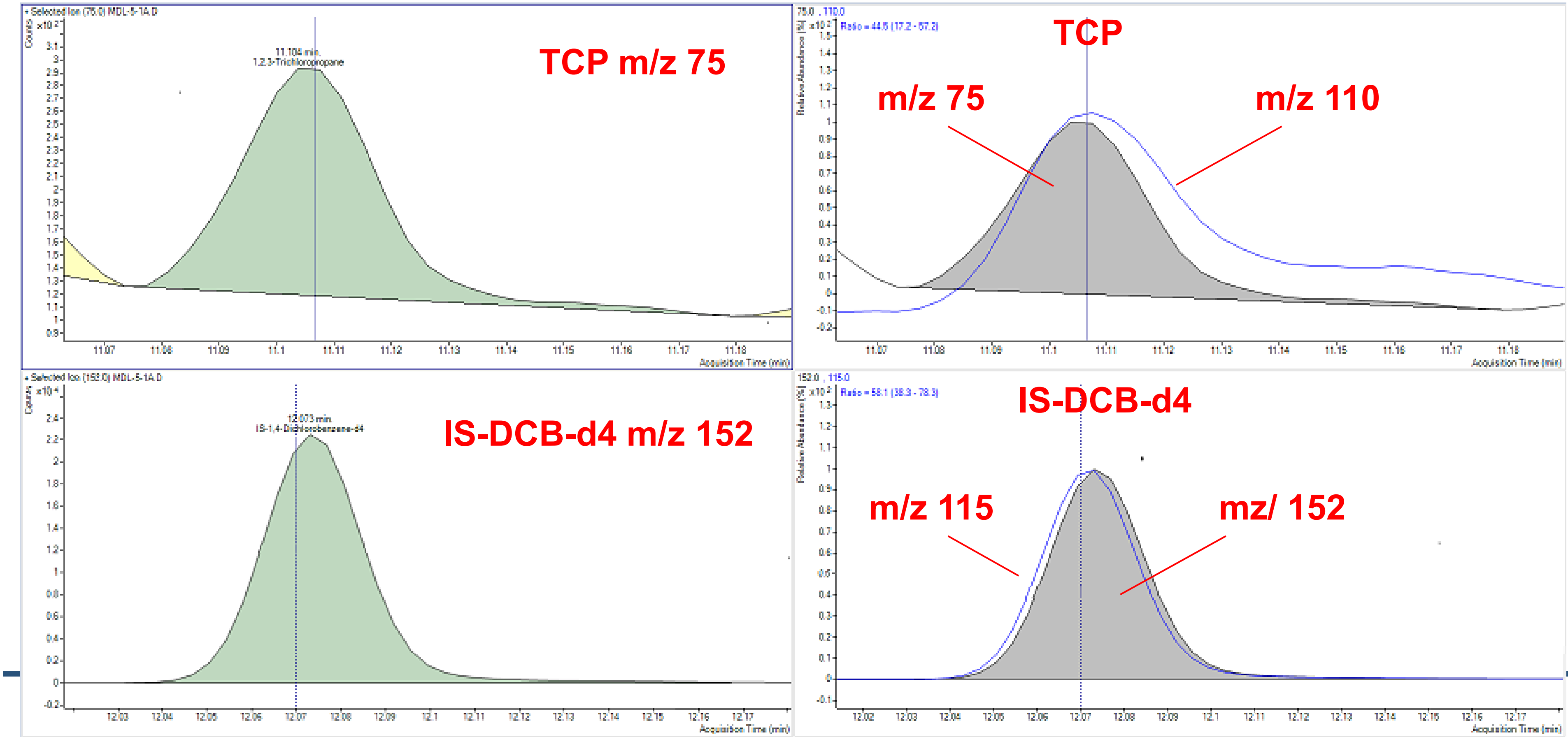
Analyte	Spiking Conc. (ng/L)	Recovery (%)	RSD (%)
TCP	20	96	5.6
		99	8.5
	20	97	1.5
		93	4.6

SRL 524M-TCP: Sensitivity (n = 7)

Analyte	Spiking Conc. (ng/L)	MDL-S (ng/L)	MDL-B (ng/L)
TCP	5.0	0.50	0.12
		0.69	---

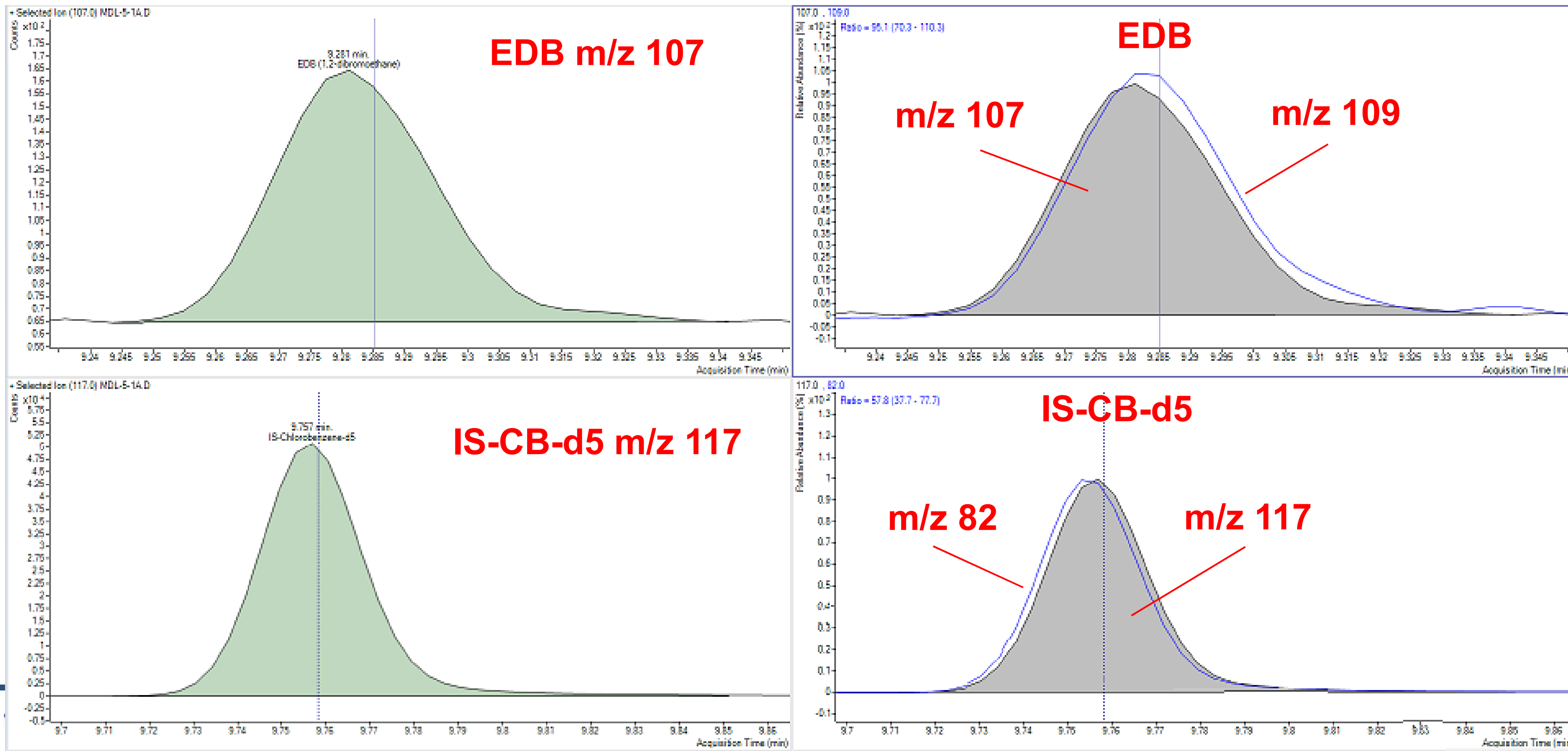
524.3 TCP at 5 ng/L

IS-1,4-Dichlorobenzene-d4 at 0.2 µg/L



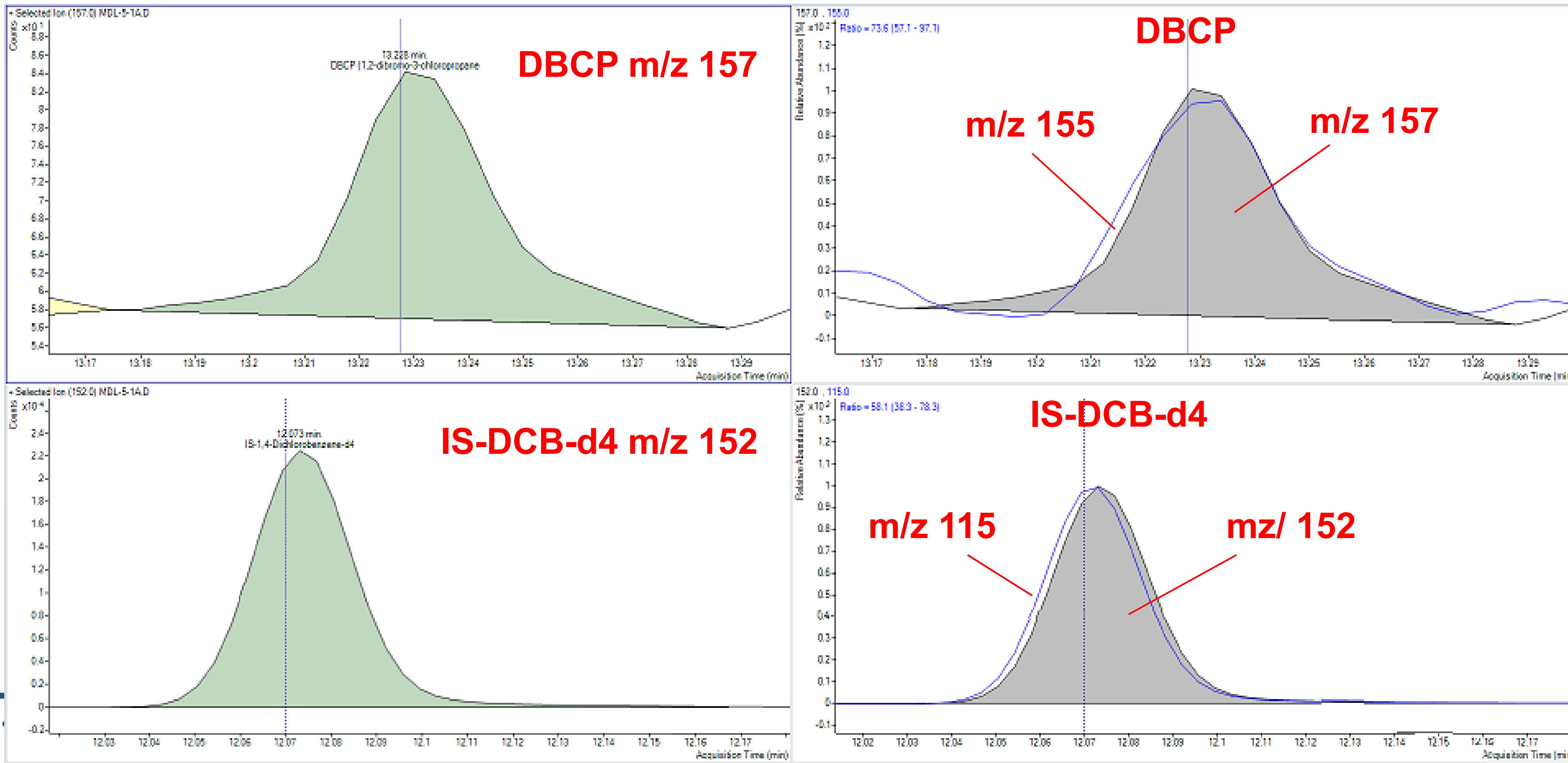
524.3 EDB at 5 ng/L

IS-Chlorobenzene-d5 at 0.2 µg/L



524.3 DBCP at 5 ng/L

IS-1,4-Dichlorobenzene-d4 at 0.2 µg/L



EPA 524.3: Accuracy and Precision

Analyte	Spiking Conc. (ng/L)	Recovery (n=4) (%)	RSD (n=4) (%)
TCP	50	89	2.6
EDB	50	88	3.0
DBCP	50	89	4.4

EPA 524.3: Sensitivity (n = 7)

PIR = Prediction Interval of Result



Analyte	Spiking Conc. (ng/L)	PIR (%)	MDL-S (ng/L)	MDL-B (ng/L)
TCP	5.0	85-137	1.4	0.36
	10	90-129	1.6	0.36
EDB	5.0	97-130	0.98	0.18
	10	90-114	1.3	0.30
DBCP	5.0	83-133	1.6	0.49
	10	85-116	1.3	0.49

PT Passing Recoveries (%) *vs.* Assigned Values



Analyte	TCP	EDB	DBCP
EPA 504.1	---	105 ERA WS-270	103 ERA WS-270
	---	96 ERA WS-264	103 ERA WS-264
SRL 524M-TCP	97 ERA WS-270	---	---
	102 ERA WS-264	---	---
EPA 524.3	100 ERA WS-270	98 ERA WS-270	102 ERA WS-270
	94 ERA WS-268	93 ERA WS-268	96 ERA WS-268
	94 ERA WS-267	90 ERA WS-267	93 ERA WS-267

Conclusions



- **EPA 504.1**
  - **Much less accurate for quantitation of lower level TCP.**
  - **Practical MRLs: ~30 ng/L for TCP and ~10 ng/L for EDB and DBCP.**
- **SRL 524M-TCP**
  - **Only approved for TCP compliance analysis in CA.**
  - **Practical MRL: ~5 ng/L for TCP. Slightly lower MRLs may be achievable.**
  - **Not adopted to some new IDC and QC requirements that have been used in recent EPA drinking water methods.**

Conclusions (cont’d)

EPA 524.3

- Included all IDC and QC requirements that have been used in recent EPA drinking water methods.
- Practical MRLs: ~5 ng/L. Slightly lower MRLs may be achievable.
- More accurate results could be expected due to the high specificity and sensitivity.
- Fully validated and certified in some states for low concentration level TCP, EDB, and DBCP testing.
- Highly recommended for drinking water compliance analysis.

Any Questions?

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