Measurement of Trihalomethanes in Water Using the Dielectric Barrier Discharge Electron Capture Detector and Headspace Extraction

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Introduction

- Discussion of different methods for THM analysis
    - Relative advantages and disadvantages
- Non-radioactive DBD-ECD
- Method of analysis
    - Headspace extraction
    - Instrumental set-up
- Results
- Future Work
- Conclusion

THM's: Trihalomethanes

- By-products of water disinfection (chlorination)
  - CF = chloroform
  - DCBM = dichlorobromomethane
  - DBCM = dibromochloromethane
  - BF = bromoform
- Suspected carcinogens
  - Regulated constituent: TTHM 80 ppb (ug/L)
  - Monitored by water distribution companies

Methods of analysis

- U.S. EPA Methods 524, 624, 8260 (P & T GC/MS)
  - Cost and complexity of instrumentation
  - Cycle time
  - Transfer of water
- U.S. EPA Methods 502, 601, 8010 (P & T GC/ELCD)
  - Cycle time
  - Transfer of water, Hall detector
- U.S EPA Method 551
  - Solvent extraction, GC/ECD
  - Simpler to implement; less transfer of water

Other Methods:

Review Paper: J. Pavon, et. al., Analytical Chimica Acta 629 (2008), 6-23

- DAI
- SPME/LPME
  - Immersion/Headspace: minimizes issue of water transfer
  - Variety of detectors: MS, ECD, Hall
  - Less expensive to implement
  - Can be fragile
- Headspace
  - Allow constituents to partition into gas phase
  - Sample the gas phase; concentration/no concentration
  - Again, variety of detectors
  - Again, less expensive to implement

Headspace/ECD

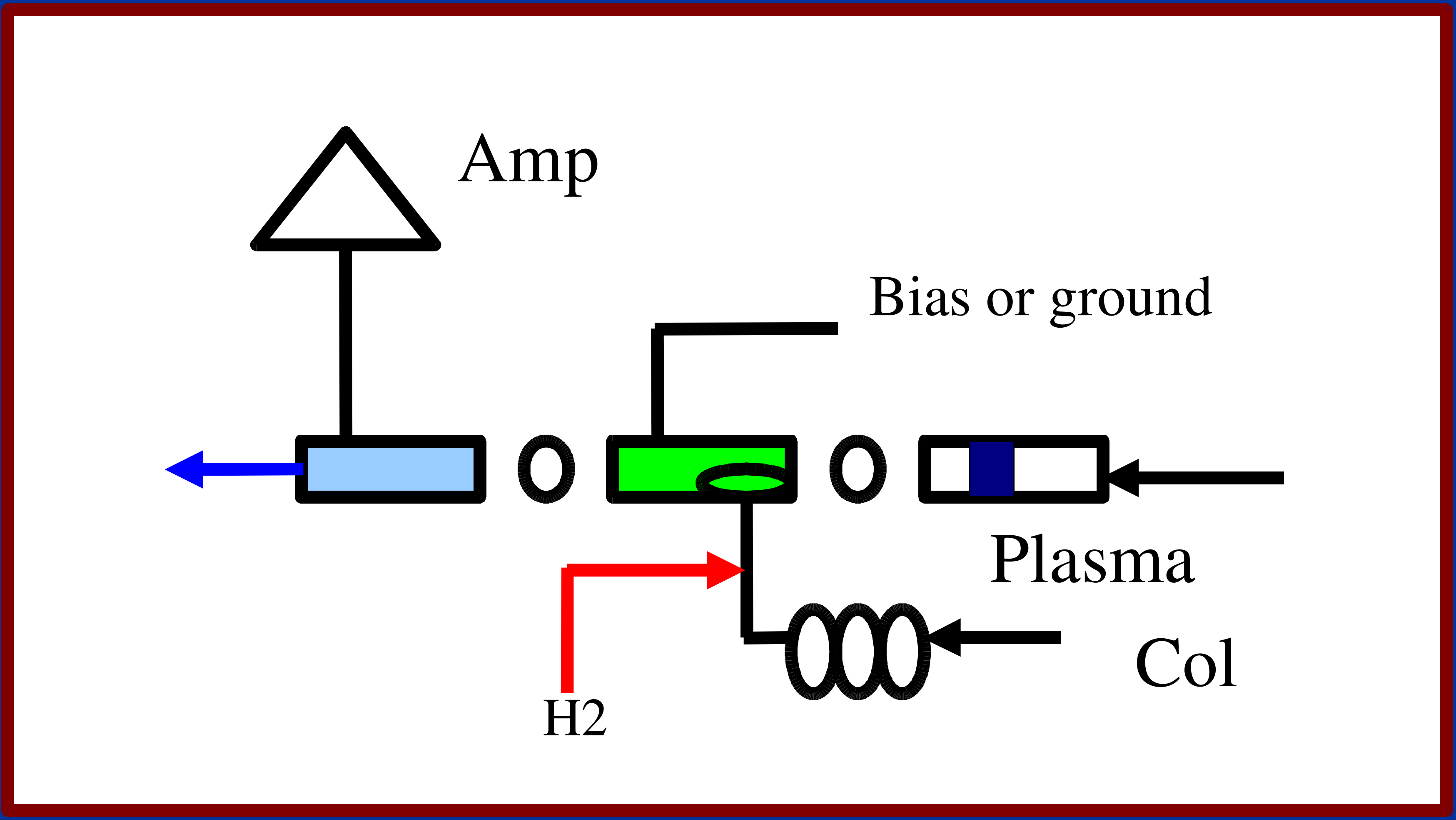
- Excellent alternative method
  - Cycle time
  - Cost and complexity of instrumentation
  - Transfer of water
  - Excellent sensitivity w/o concentration
- Main disadvantage: use of ECD
  - Limited linearity
  - Varying responses (not so bad here)
  - Radioactive Source (licensing, monitoring disposal, cleaning) - transfer of water

Non-rad ECD solves biggest hurdle

Use DBD plasma to replace radioactive source

- Dielectric Barrier Discharge plasma
  - HV A/C discharge across a dielectric barrier (glass tube)
  - Non-thermal discharge – each discharge is limited
  - Low electrode wear
  - Large electrode; multiple discharges
- Because of the DBD physics
  - Windowless, non-radioactive source
  - Forgiving source
  - Simple power supply

ECD Schematic



DBD-ECD Advantages (DBD); Disadvantages(ECD), except...

- Advantages:
  - Non-radioactive – don't care about water as much
  - Highly sensitive
  - Able to operate without getters
  - Able to use conventional ECD electrometers
- Disadvantages (mostly the same as regular ECD)
  - Widely varying sensitivity, limited linearity
  - Requires two gas supplies (helium and very low flow hydrogen), clean gases, leak free
  - *Good dopant flow control*

Ideal for headspace/THM

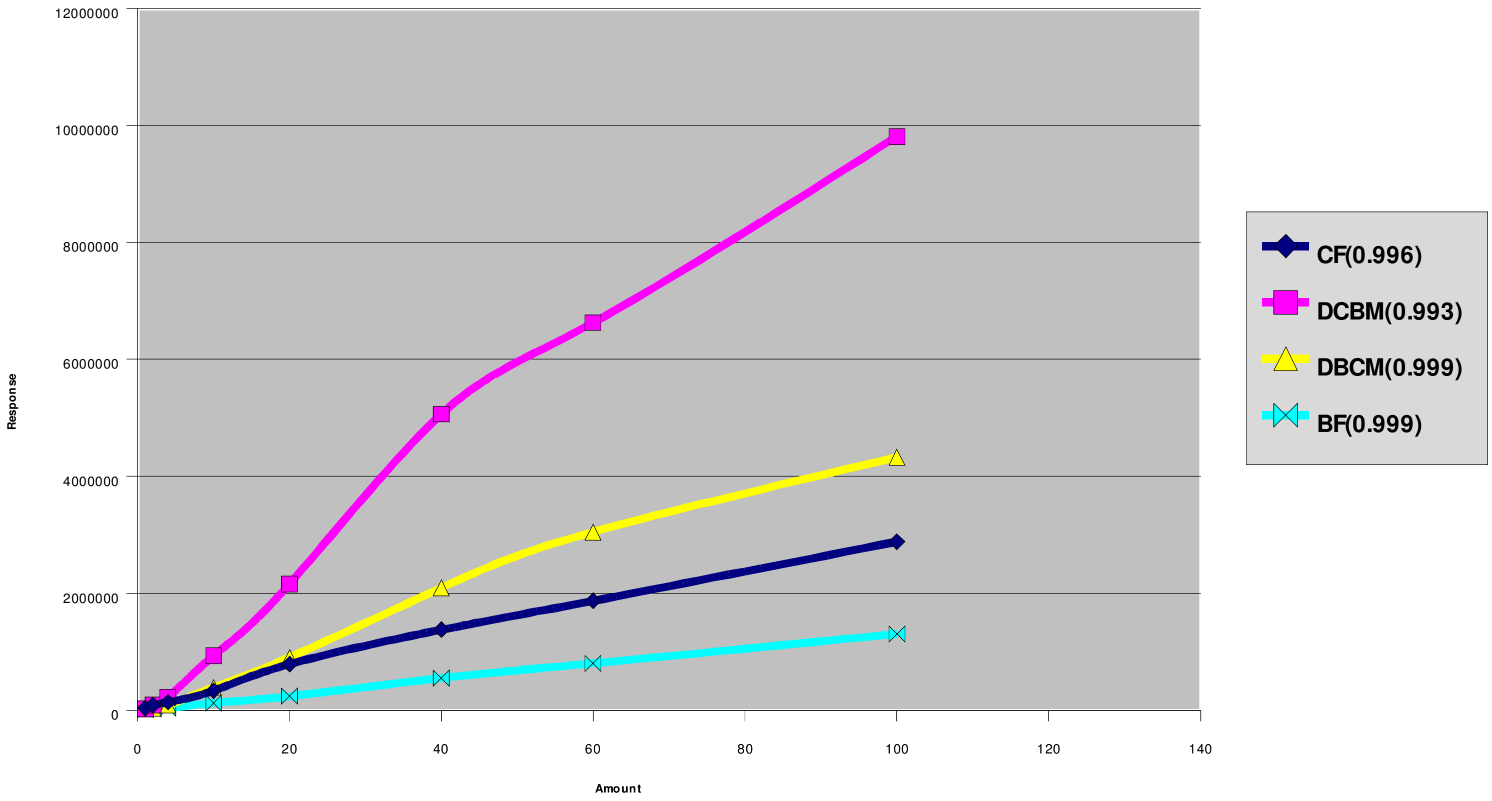
Method of analysis: extraction

- Emphasis on ease of use and speed
  - All materials readily available
  - Inexpensive set-up
  - Short cycle time (under 12 minutes)
- Headspace Extraction
  - 15 mL water in “20” mL VOA vial
  - Heated for 10 min @50 C
  - Shaken for 1 min
  - 4mL room air added; 3 mL removed
  - Aliquot transferred to GC using syringe
- No concentration

Method of analysis: Instrumental

- GC Method
  - HP 5890A
  - 6-Port valve, 1 mL loop
  - 30 meter RTX-VMS, 0.25 id X 1.4 film
  - Flow rate: 6 mL/min (high)
  - Oven program: 35C/6 min/14C/min/105 C/3 min
- Detector
  - DBD-ECD, 200 C
  - H2 flow 4 ml/min, rxn flow He 40 mL/min
  - Vp = 5 V, iP = 0.28 A
  - Electrometer: Stock HP ECD electrometer in N2 mode

Calibration Curve, 1-100 ppb

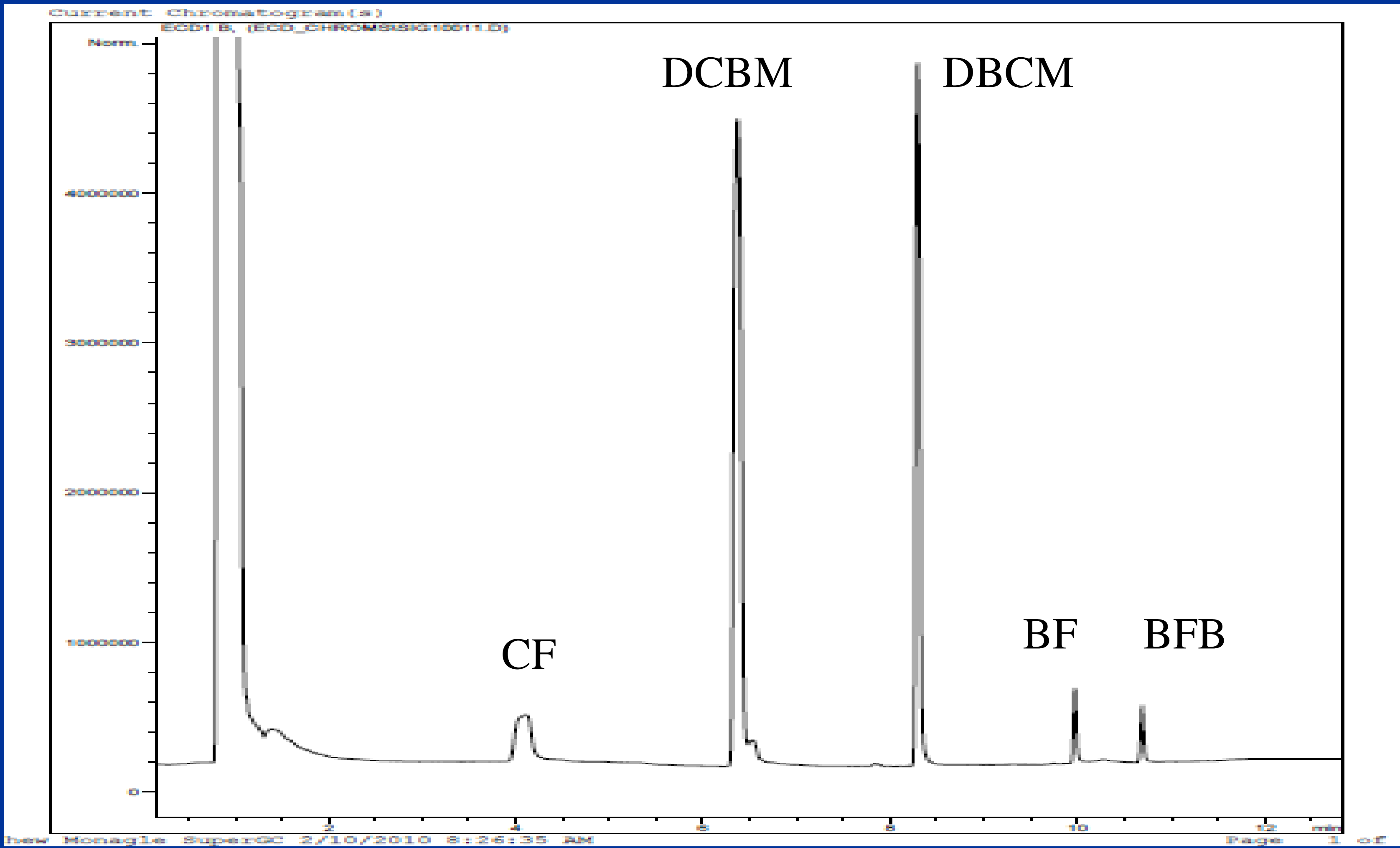


Only 2 orders but covers the range of interest

Method Detection Limit Study
(7 replicates spiked at 1.3 ppb)

	CF	DCBM	DBCM	BF
Std Dev	0.16	0.12	0.13	0.1
Avg	1.3	1.43	1.44	1.12
Rsd	0.12	0.08	0.09	0.09
Stdnt T	3.14	3.14	3.14	3.14
MDL*	0.5	0.37	0.41	0.33

Local Drinking Water: SE Abq.



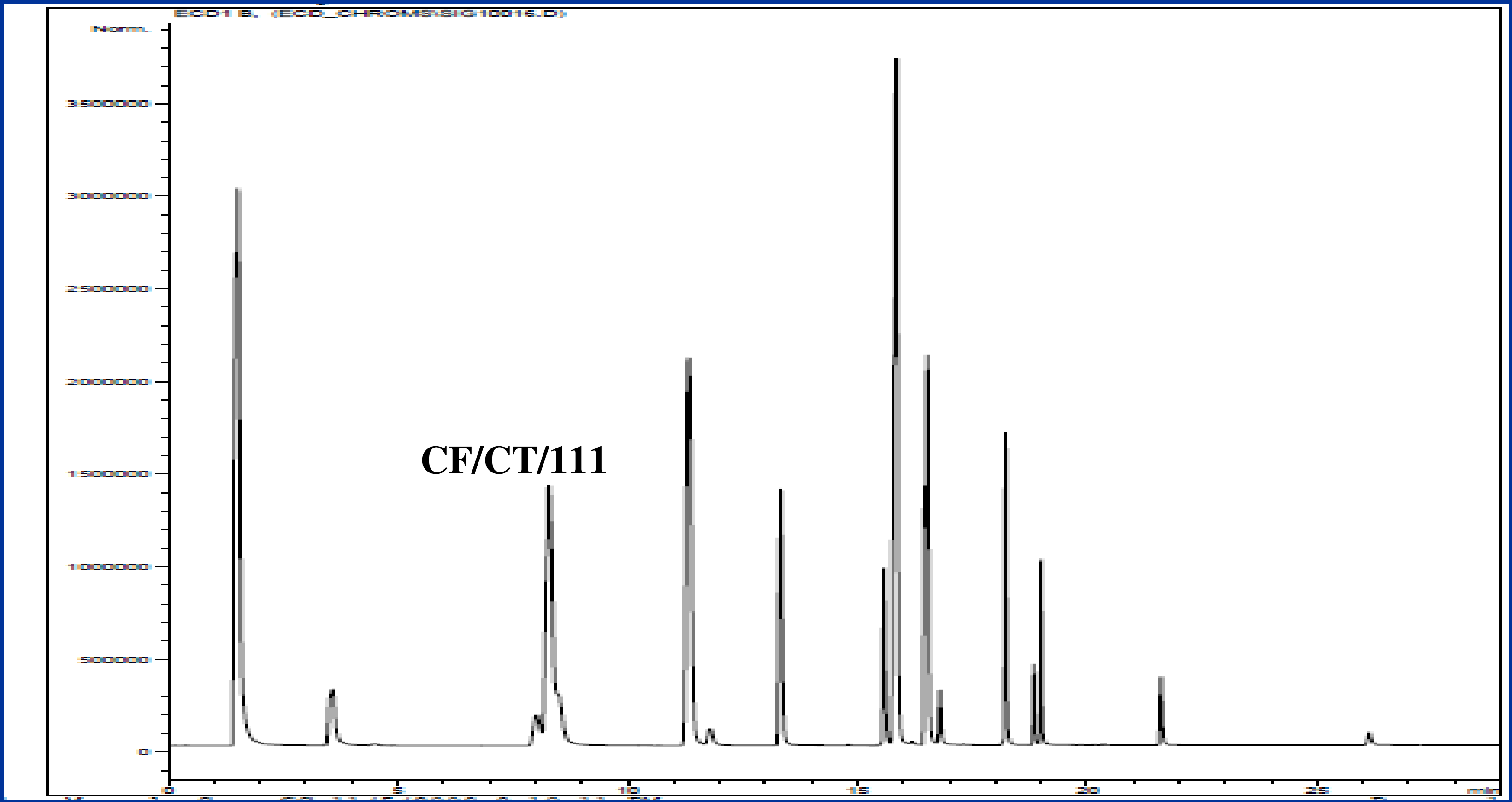
CF peak shape; CF much lower than expected; BFB response(270 ppb); lots of empty space.

Various Albuquerque Water Samples

	CF	DCBM	DBCM	BF	TTHM
West ABQ	3.62	6.23	11.64	6.93	28.41
West ABQ (dup)	3.02	5.62	10.96	6.45	26.04
SE Abq	4.85	7.36	9.55	3.07	24.83
Pool 3X	45.99	-0.26	-0.16	-0.59	44.97

Less CF than expected; higher values than stated in Albuquerque Water reports, follows same distribution trend; Swimming pool water all CF

551.1 Standard (in air)



Another application for the DBD-ECD; note the significant difference in response

Further work

- Better internal standard would be useful
  - BNB or CIB possible candidate
- Improve the headspace extraction
  - Investigate the addition of salt
- Investigate the use of nitrogen dopant
  - Better sensitivity or linearity?
- Beta test unit in local laboratory
  - Side by Side comparison of samples
  - Real users evaluating the DBD-ECD

Conclusion

- Headspace extraction/ECD is an attractive alternative to purge and trap extraction for THM's
  - Simple method with sufficient sensitivity
  - Short cycle times
- DBD-ECD effective substitute for radioactive ECD
  - Provides low detection limits
  - Good linearity over the range of interest
  - Specificity
  - Eliminates the issues of radioactive source