Chloroform Extraction of Iodine in Seawater Method Development

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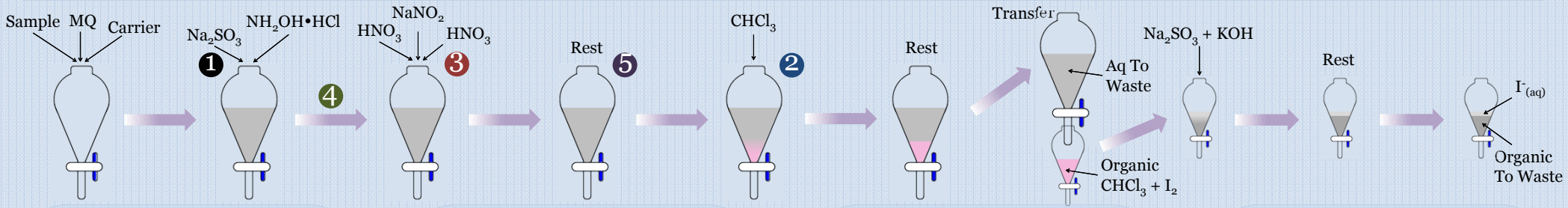
Abstract: The extraction of iodine from seawater is used as a means of analyzing the concentration and isotopic ratios of iodine at different locations in the ocean. This has practical applications in the testing of discharge from nuclear fuel reprocessing plants, tracing of ocean currents, and testing areas for potential environmental and health impacts. One of the current methods used is a separation extraction involving chloroform ($CHCl_3$). This method is lengthy (almost an hour per sample) and does not guarantee 100% recovery of the iodine in the water. This research seeks to optimize the existing protocol for efficiency while maintaining or improving recovery. We assessed each methodological change qualitatively using a color scale (I_2 in $CHCl_3$) and quantitatively using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

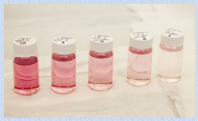


Original Method:

- 250mL sample + 250mL Milli-Q (MQ)
- 1mL carrier (known [I^-]) + shake 1 min
- 10mL .25M Na_2SO_3 + shake 1 min
- 10mL .25M $NH_2OH•HCl$ + shake 1 min
- 1mL concentrated HNO_3 + shake 1 min
- 10mL .25M $NaNO_2$ + shake 1 min
- 1mL conc. HNO_3 + shake 1 min
- Rest 15 min
- 50mL $CHCl_3$ + shake 1 min
- Rest 10 min
- Transfer organic, aqueous to waste
- 5mL Na_2SO_3 + KOH + shake 1 min
- Rest 10 min
- Organic to waste, transfer aqueous
- Dilute aqueous to ~.6µg/L with tetramethylammonium hydroxide (TMAH), tellurium, and MQ
- Run on ICP-MS for I^- concentration
- Recovery of I_2: ~60%

Assessment of New Methods:

- Color Scale:
  - Qualitative analysis
  - 10 (~0.10 mg/mL)
  - 7 (~0.07 mg/mL)
  - 5 (~0.05 mg/mL)
  - 3 (~0.03 mg/mL)
  - 1 (~0.01 mg/mL)



- ICP-MS:
  - Quantitative analysis
  - % recovery from carrier + seawater

Method Development 1

Changes in Concentrations

Trial	Na_2SO_3 (.5M)	$NH_2OH•HCl$ (.5M)	$NaNO_2$ (.5M)	Color (on Scale)	Recovery (%)
MD 1_1	5mL	5mL	5mL	<1	
MD 1_2	5mL + 5mL		5mL	1	
MD 1_3	4mL + 4mL		5mL	2	
MD 1_4	3mL + 3mL		5mL	2	
MD 1_5	5mL + 5mL		6mL	2	
MD 1_6	5mL + 5mL		7mL	2	
MD 1_7	3mL + 3mL		7mL	2	
MD 1_8	5mL	0	5mL	>1	
MD 1_9	0	5mL	5mL	1	

- 10mL of .25M solution = 5mL of .5M solution
- Both Na_2SO_3 & $NH_2OH•HCl$ oxidize IO_3^- to I^-

$IO_3^- + 3HSO_3^- \rightarrow I^- + 3SO_4^{2-} + 3H^+$

$IO_3^- + 3NH_2OH \rightarrow 3NO_2^- + 3H^+ + 2I^- + 3H_2O$

- Should be able to be added at once with 1 shake
- Can only one be used?
- NO_2^- addition is crucial to extraction because I_2 is more soluble in $CHCl_3$

$2I^- + 2NO_2^- + 2H^+ \rightarrow I_2 + 2H_2O + 2NO$

Method Development 2

Chloroform Double Extraction

Trial	$CHCl_3$	1st Rest	2nd Rest	Color (on Scale)	Recovery (%)
MD 2_1	25mL x 2	5 min	5 min	1	
MD 2_2	25mL x 2	2 min	2 min	<2	

- Some I_2 left in aq. 2 $CHCl_3$ additions should recover more because of the partitioning coefficient

Method Development 3

Concentrated HNO_3 Additions

Trial	1st Add. HNO_3	$NaNO_2$ (.5M)	2nd Add. HNO_3	Color (on Scale)	Recovery (%)
MD 3_1	2mL	5mL	0mL	1	
MD 3_2	0mL	5mL	2mL	>1	
MD 3_3	2mL	5mL	2mL	2	
MD 3_4	.5mL	5mL	.5mL	1	

- I^- to I_2 reaction needs acidic env., how acidic?

Method Development 4

Adding a 4th Rest

Trial	1st Rest (After Na_2SO_3 + $NH_2OH•HCl$)	2nd Rest (After HNO_3 + $NaNO_2$)	Color (on Scale)	Recovery (%)
MD 4_1	15min	15min	<1	
MD 4_2	15min	10min	<1	
MD 4_3*	15min	5min	2	
MD 4_4	10min	5min	<2	
MD 4_5	5min	5min	1	
MD 4_6	10min	2min	2	

*Results of 2nd trial, first were thrown out

- IO_3^- to I^- rxns are slow & inhibited by NO_2^-
- I^- to I_2 rxn is faster, will a break increase recovery?

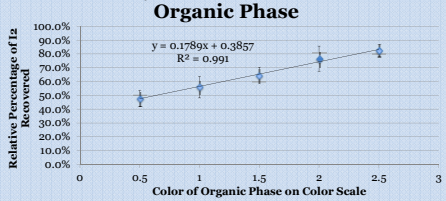
Method Development 5

Changes in Current Rest Times

Trial	1st Rest	2nd Rest	3rd Rest	Color (on Scale)	Recovery (%)
MD 5_1	20min	10min	10min	1	
MD 5_2	15min	2min	10min	>1	
MD 5_3	15min	10min	2min	1	

Conclusion:

Recovery % of Iodine vs. Color of Organic Phase



Two main aspects of the data were examined:

1. Can the color scale be used as an accurate immediate assessment of I_2 recovery? The color scale depicts an approx. 10% recovery increase for each 0.5 visual increase. It is qualitative, but works as a quick check.
2. Which methodological changes would improve efficiency and recovery of I_2? The changes that produced greater I_2 recovery were decreasing the $NaSO_3$ and $NH_2OH•HCl$ while keeping $NaNO_2$ the same (MD 1_4) and adding a rest after $NH_2OH•HCl$ and reducing the rest after the 2nd HNO_3 addition(MD 4_6).

Combining the most effective trials for each change while minimizing time gave 80-85% recovery rates while shortening the entire process by 20 minutes.

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