

Chloroform Extraction of Iodine in Seawater Method Development

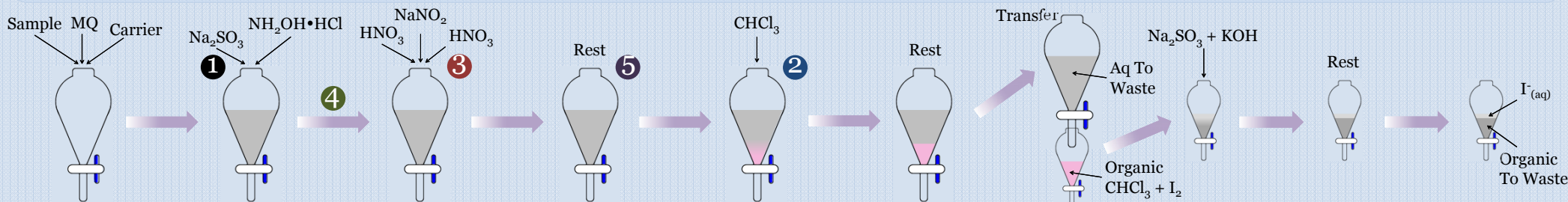
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Abstract: The extraction of iodine from seawater is used as a means of analyzing the concentration and isotopic ratios of iodine at different locations in the ocean. This has practical applications in the testing of discharge from nuclear fuel reprocessing 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 (CHCl₃). 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 (I₂ in CHCl₃) 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 Na₂SO₃ + shake 1 min
- 10mL .25M NH₂OH·HCl + shake 1 min
- 1mL concentrated HNO₃ + shake 1 min
- 10mL .25M NaNO₂ + shake 1 min
- 1mL conc. HNO₃ + shake 1 min
- Rest 15 min
- 50mL CHCl₃ + shake 1 min
- Rest 10 min
- Transfer organic, aqueous to waste
- 5mL Na₂SO₃ + 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 I₂: ~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



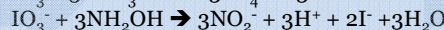
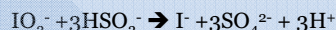
Method Development 1

Changes in Concentrations

Trial	Na ₂ SO ₃ (.5M)	NH ₂ OH·HCl (.5M)	NaNO ₂ (.5M)	Color (on Scale)	Recovery (%)
MD 1_1	5mL	5mL	5mL	<1	~10
MD 1_2	5mL + 5mL		5mL	1	~20
MD 1_3	4mL + 4mL		5mL	2	~30
MD 1_4	3mL + 3mL		5mL	2	~30
MD 1_5	5mL + 5mL		6mL	2	~30
MD 1_6	5mL + 5mL		7mL	2	~30
MD 1_7	3mL + 3mL		7mL	2	~30
MD 1_8	5mL	0	5mL	>1	~40
MD 1_9	0	5mL	5mL	1	~20

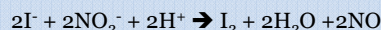
- 10mL of .25M solution = 5mL of .5M solution

- Both Na₂SO₃ & NH₂OH·HCl oxidize IO₃⁻ to I⁻



- Should be able to be added at once with 1 shake
- Can only one be used?

- NO₂⁻ addition is crucial to extraction because I₂ is more soluble in CHCl₃



Method Development 2

Chloroform Double Extraction

Trial	CHCl ₃	1 st Rest	2 nd Rest	Color (on Scale)	Recovery (%)
MD 2_1	25mL x 2	5 min	5 min	1	~20
MD 2_2	25mL x 2	2 min	2 min	<2	~10

- Some I₂ left in aq. 2 CHCl₃ additions should recover more because of the partitioning coefficient

Method Development 3

Concentrated HNO₃ Additions

Trial	1 st Add. HNO ₃	NaNO ₂ (.5M)	2 nd Add. HNO ₃	Color (on Scale)	Recovery (%)
MD 3_1	2mL	5mL	0mL	1	~20
MD 3_2	0mL	5mL	2mL	>1	~40
MD 3_3	2mL	5mL	2mL	2	~30
MD 3_4	.5mL	5mL	.5mL	1	~20

- I⁻ to I₂ reaction needs acidic env., how acidic?

Method Development 4

Adding a 4th Rest

Trial	1 st Rest (After Na ₂ SO ₃ + NH ₂ OH·HCl)	2 nd Rest (After HNO ₃ + NaNO ₂)	Color (on Scale)	Recovery (%)
MD 4_1	15min	15min	<1	~10
MD 4_2	15min	10min	<1	~10
MD 4_3*	15min	5min	2	~30
MD 4_4	10min	5min	<2	~20
MD 4_5	5min	5min	1	~20
MD 4_6	10min	2min	2	~30

*Results of 2nd trial, first were thrown out

- IO₃⁻ to I⁻ rxns are slow & inhibited by NO₂⁻
- I⁻ to I₂ rxn is faster, will a break increase recovery?

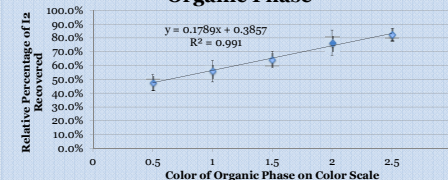
Method Development 5

Changes in Current Rest Times

Trial	1 st Rest	2 nd Rest	3 rd Rest	Color (on Scale)	Recovery (%)
MD 5_1	20min	10min	10min	1	~20
MD 5_2	15min	2min	10min	>1	~40
MD 5_3	15min	10min	2min	1	~20

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 I₂ 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 I₂? The changes that produced greater I₂ recovery were decreasing the Na₂SO₃ and NH₂OH·HCl while keeping NaNO₂ the same (MD 1_4) and adding a rest after NH₂OH·HCl and reducing the rest after the 2nd HNO₃ 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.

Acknowledgements:

This material is based upon work supported by the S.D. Bechtel, Jr. Foundation and by the National Science Foundation under Grant No. 0952013 and Grant No. 0934931. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the S.D. Bechtel, Jr. Foundation or the National Science Foundation. This project has also been made possible with support of the National Marine Sanctuary Foundation. The STAR program is administered by the Cal Poly Center for Excellence in Science and Mathematics Education (CESaME) on behalf of the California State University (CSU). This work is performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Release #: LLNL-P087-570292