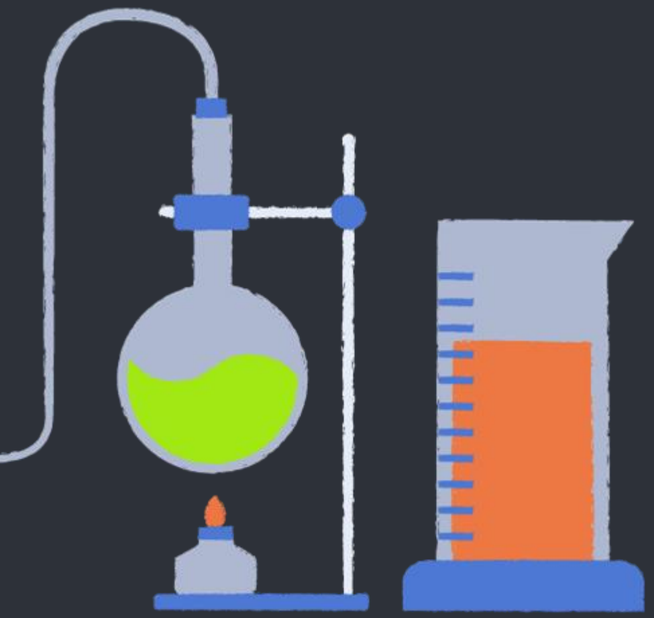
Determination of Methylparaben in Lotion by Capillary Electrophoresis



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ABSTRACT

- Solvent extraction of methylparaben from hand lotion using methanol.
- Analysis by capillary electrophoresis (CE).

- First sample set had concentrations outside calibration curve.
- More dilute samples were extracted and prepared.
- Spikes added to prepared samples for recovery studies.

- 2516 ppm ± 5.21% methylparaben in lotion (undiluted)
- Average percent recovery: 165.8% (inaccurate)

WHAT IS METHYLPARABEN?

Figure 1. Vaseline intensive care aloe vera hydration lotion sample used for analysis and ingredient list.

- Parabens, including methylparaben, are common preservatives[2,3].
- They prevent growth of microorganisms in cosmetic projects[2,3].
- Highly speculated to have adverse health effects[2].
- No strong evidence to support these claims.

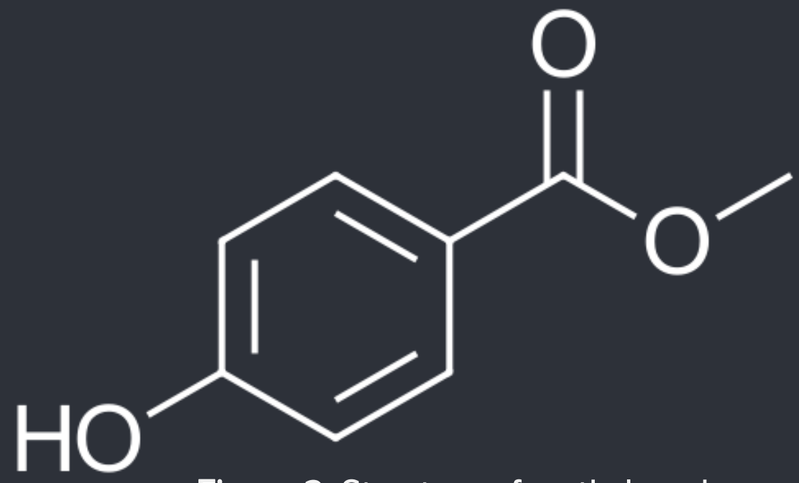

Figure 2. Structure of methylparaben.

CAPILARY ELECTROPHORESIS

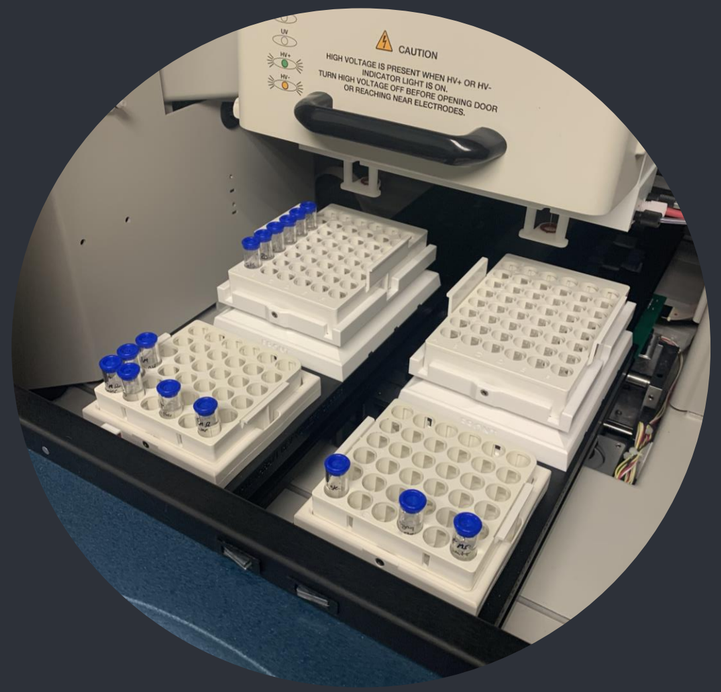

Figure 3. Inside of CE instrument showing samples in sample trays.

- An analytical separation method.
- Solutes are separated based on relative mobility through a silica capillary under a strong electric field[1,4].
- Utilizes a buffer to generate flow through the capillary[1,4].
- A detector near the negative cathode is utilized. This experiment used an ultraviolet detector.
- Separation of neutral molecules can be more difficult.

EXPERIMENTAL: sample and standard preparation

Sample and Reagents:

- Vaseline intensive care aloe vera hydration lotion
- 1000 ppm methylparaben stock solution
- 20 mM sodium borate buffer
- Methanol

Standard Prep:

- Pipetted appropriate volumes (see Table 1) of 1000 ppm methylparaben stock solution into CE vials.
- Diluted to 1.00 mL with methanol.

Table 1. Volume of 1000 ppm methylparaben solution used to prepare standard solutions of various concentrations in ppm.

Vial #	Concentration methylparaben (ppm)	Volume 1000 ppm methylparaben (μL)	Volume Methanol (μL)	Total volume (μL)
1	1.0	1.0	999.00	1000.00
2	5.0	5.0	995.00	1000.00
3	10.0	10.0	990.00	1000.00
4	20.00	20.00	980.00	1000.00
5	25.00	25.00	975.00	1000.00

Sample Prep:

- Based on method from literature[2].
- Weighed 0.6 g lotion into 15 mL centrifuge tube.
- Diluted lotion with methanol.
  - Week 1: 1.6 mL into ~ 0.6000 g lotion
  - Week 2: 9.6 mL into 0.6000 g lotion &10x dilution by 10.00 mL volumetric flask
- Vortexed tube for 3 min.
- Centrifuged samples for 10 min at 6000 rpm to separate solid from aqueous layer.
- Filtered approximately 1 mL of aqueous sample through 0.45 μm syringe filter into CE vials.

Figure 4. Lab selfie with sample vials.

EXPERIMENTAL: Instrumental Parameters

Table 2. Optimized instrumental parameters for capillary electrophoresis (CE) analysis of methylparaben in lotion.

Capillary:	Fused silica, 50 μm I.D. x 375 μm O.D. x 50 cm total length (40 cm to detector)
Operating Temperature:	25 °C
Run Time:	15 min
Detection:	UV, 214 nm (direct absorbance)
Rinse Pressure (0.1 M NaOH):	20 psi for 3.0 min
Rinse Pressure (water):	20 psi for 1.0 min
Rinse Pressure (rinse buffer):	20 psi for 3.0 min
Injection Pressure:	1 psi for 5.0 s
Separation Voltage:	20 kV
Polarity:	Normal
Buffer Concentration:	20 mM
Buffer pH:	9.51

Figure 5. SCIEX P/ACE System MDQ Plus capillary electrophoresis system used for analysis.

DATA AND RESULTS

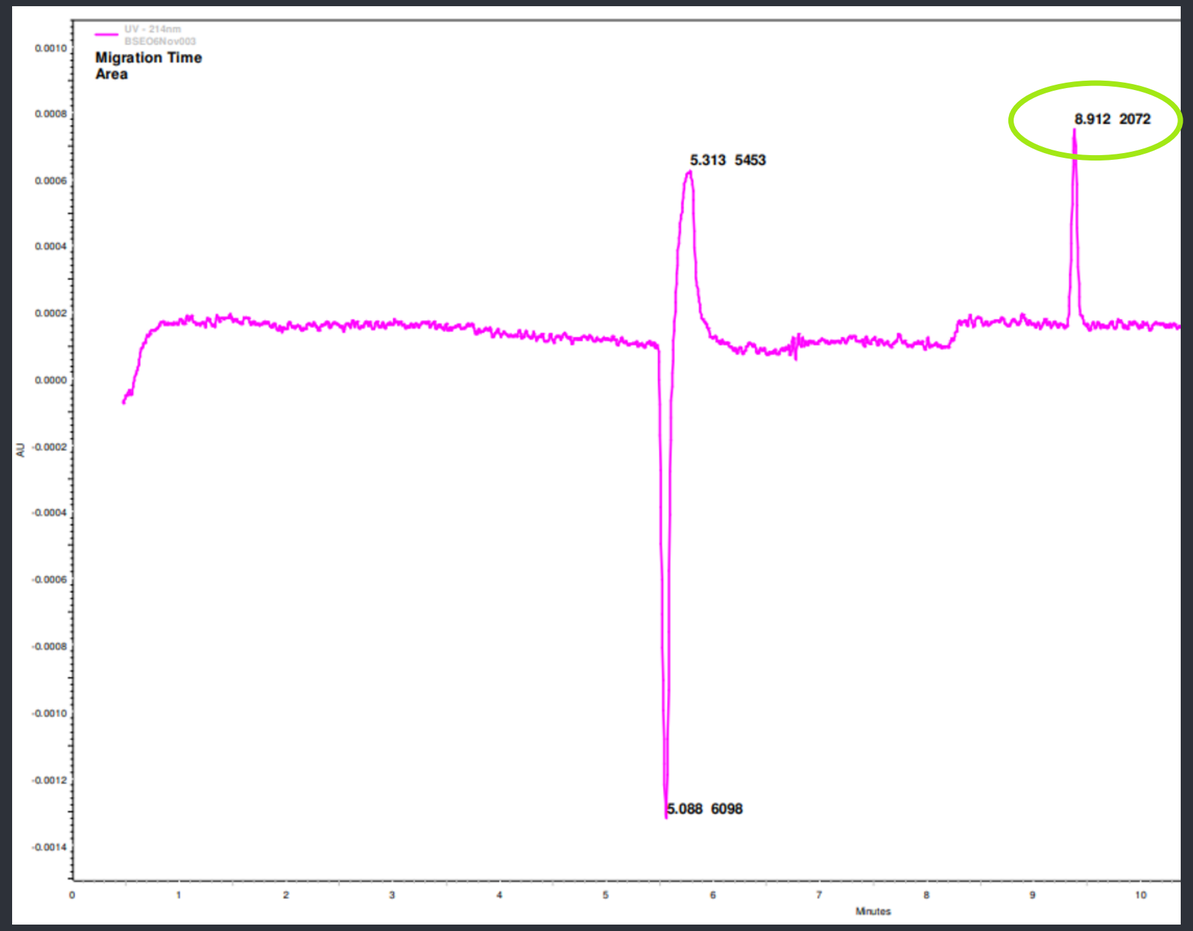

Figure 7. Electropherogram for standard 3 with 10.00 ppm methylparaben.

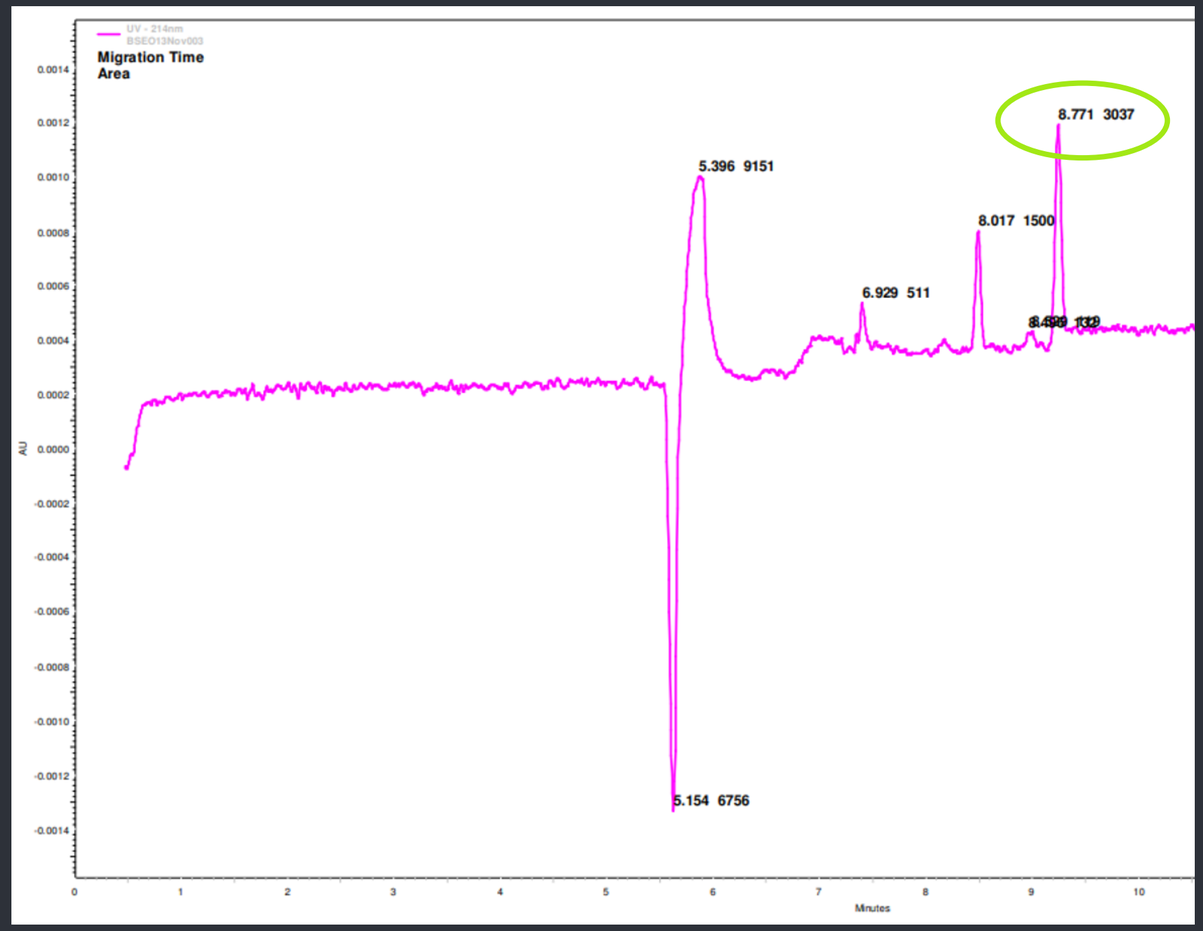

Figure 8. Electropherogram for unspiked lotion sample ran on week 2.

DATA AND RESULTS

Table 3. CE results of methylparaben standards used to generate the calibration curve.

Standard #	[methylparaben] (ppm)	Migration Time (min)	Peak Area
1	1.00	8.917	306
2	5.00	8.871	1128
3	10.00	8.912	2072
4	20.00	8.988	3885
5	25.00	8.921	5211

Table 4. CE results of unknown solutions, including week one unknowns, and recovery studies samples from week two.

Sample	Mass Lotion (g)	Migration Time (min)	Peak Area
Week 1 unk 1	0.6303	8.738	166411
Week 1 unk 2	0.6017	8.683	163050
Week 1 unk 3	0.6041	8.838	163618
Unspiked	0.6000	8.771	3037
80 % spiked	0.6000	8.775	6595
100 % spiked	0.6000	8.787	7987
120 % spiked	0.6000	8.838	7573

DATA AND RESULTS

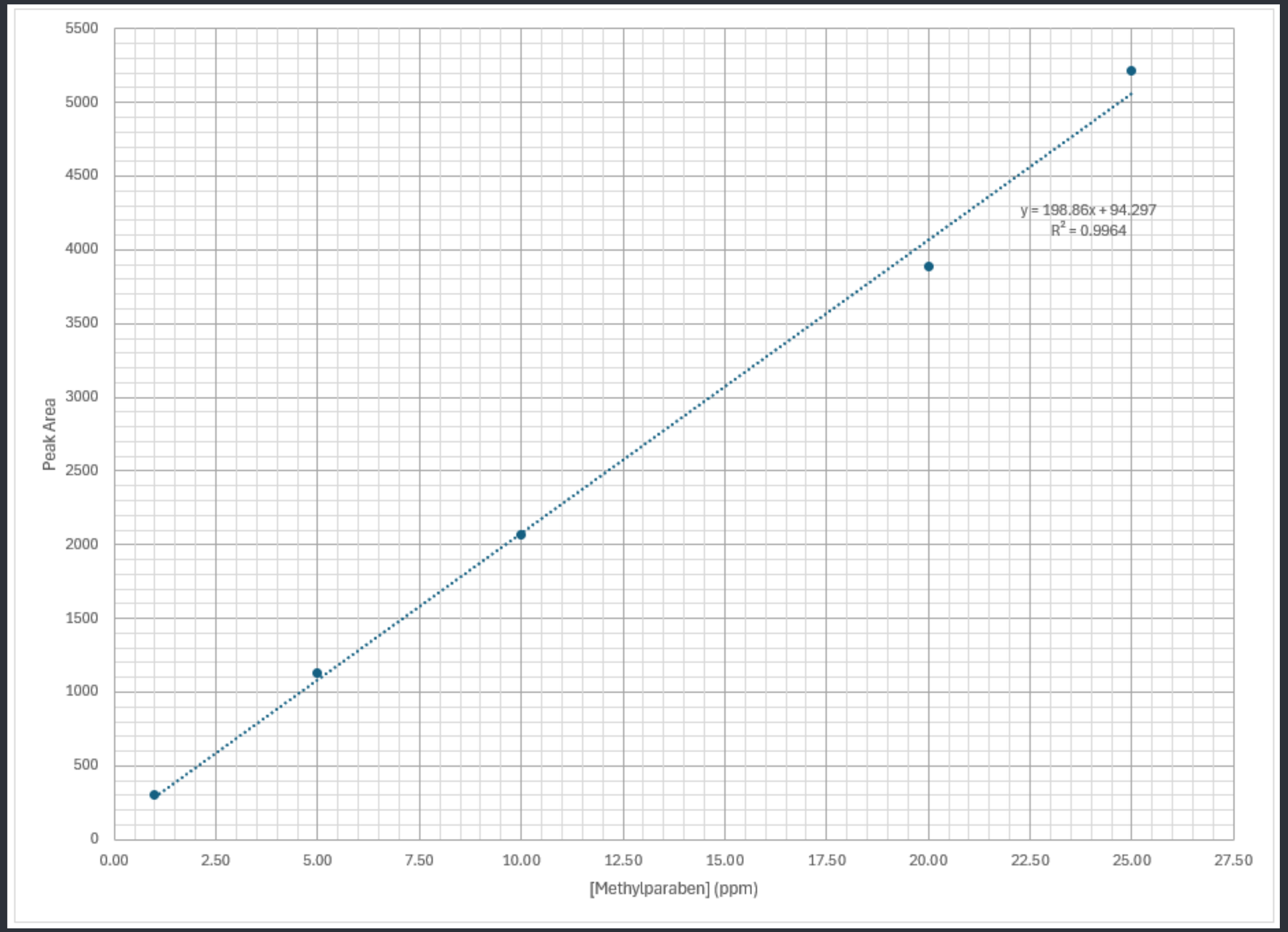

Figure 9. Calibration curve of peak areas as methylparaben concentration (ppm) in standard solutions increases.

DATA AND RESULTS

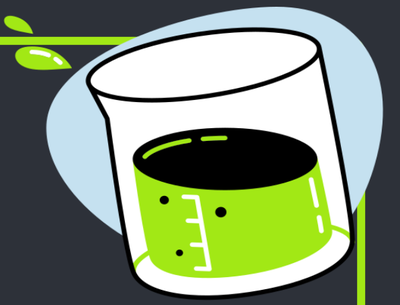

Table 5. Recovery studies results, including the spike volume and concentration, measured concentration and percent recovery.

Sample	Vol 1000 ppm methylparaben stock added (μL)	[Methylparaben] added (ppm)	[Methylparaben] (ppm)	% recovery
Unspiked	0	0.00	14.80	-
80% spiked	10.8	10.68	32.69	167.5%
100% spiked	13.5	13.32	39.69	186.9%
120% spiked	16.2	15.94	37.61	143.1%

Table 6. Summary of results for determination of methylparaben in unspiked lotion sample by CE including experimental concentrations (diluted and undiluted), % RSD, equation of the line, R^2, and uncertainty values.

Experimental methylparaben content in diluted sample =	14.80 ppm
Experimental methylparaben content in undiluted sample =	2516 ppm ± 5.21%
mg methylparaben per g lotion =	2.516 mg/g
% RSD =	5.2%
Equation of the line =	y = 198.86x + 94.297
R^2 =	0.9964
Uncertainty of the y-intercept (S_b) =	104.33
Uncertainty of the slope (S_m) =	6.88 ppm^{-1}
Uncertainty of the unknown (S_x) =	0.77 ppm

DISCUSSION

Week One:

- Spent optimizing experimental design and running standard solutions (1 ppm – 100 ppm).
- 4 standard solutions successful and 2 inconclusive (50 ppm & 100 ppm).
- Lotion samples outside concentrations of standard solutions, so week 2 samples diluted.

Week Two:

- Spent conducting recovery study by running spiked and unspiked samples.
- Unspiked sample found to be within calibration curve, but methylparaben concentrations still too high for spiked samples to be accurately determined using equation of the line. Spikes would have been accounted for if higher concentrated standards worked.
- Extraction procedure modified from literature was found to be very successful[2].

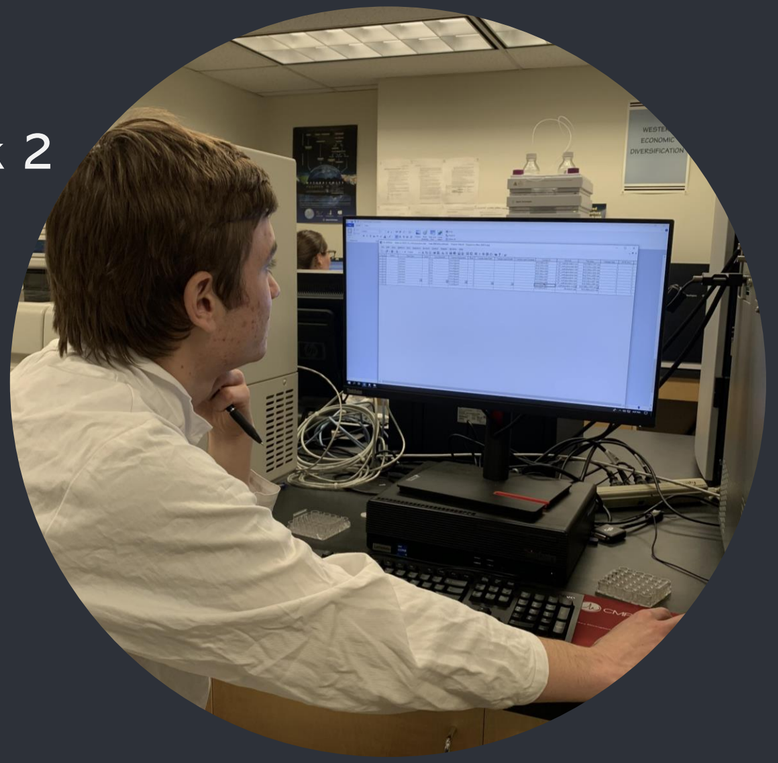

Figure 10. Using CE software to set up experimental method and sequence.

DISCUSSION

Results:

- [methylparaben] unspiked sample determined to be 2516 ppm ± 5.21% or 2.516 mg/g (see Table 6).
- R^2 = 0.9964 showing good linearity (see Table 6).
- Peak areas for week 1 samples greater than standards, (see Table 4), so inaccurate and not included.
- Average percent recovery of 165.8 % (see Table 5). Inaccurate because spiked samples were outside calibration curve and possible interference from propylparaben.
- Paraben concentrations in lotion not on label so % error was not calculated.
- Literature values of [methylparaben] range from 0.939 – 4 mg/g[3,5].

Sources of Error:

- Micropipettes not being calibrated.
- Methylparaben signal in CE being skewed by presence of other parabens in lotion.
- Glassware (beakers and volumetric flasks) not being calibrated.

FUTURE WORK

- Higher concentrated standards could be run again to account for spiked samples. Would increase accuracy recovery study data.
- Unspiked lotion sample could be run again in triplicate to minimize error.
- CE could be run using micelles to determine concentrations of multiple different parabens.
- More paraben containing lotion samples from brands other than Vaseline could be analyzed using CE and samples could be compared using PCA.

CONCLUSION

- Concentration of methylparaben in Vaseline intensive care aloe vera hydration lotion determined to be 2516 ppm ± 5.2%.
- Approximately double the concentration found in other hand creams but under recommended limits[3,5].
- Literature [methylparaben]s of two hand creams were 0.977 ± 0.156 mg/g and 0.939 ± 0.159 mg/g[5].
- Recommended concentration: 4 mg/g[3].
- Concentration could be high due to presence of parabens other than methylparaben, like propylparaben.
- Extraction procedure to extract parabens from lotion was found to be successful.

REFERENCES

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3. European Scientific Committees. **2011**. Parabens used in cosmetics. https://ec.europa.eu/health/scientific_committees/docs/citizens_parabens_en.pdf (accessed November 16, 2024)

4. Weinberger, R. Practical Capillary Electrophoresis, 2nd ed., Academic Press: New York, 2000.

5. Ye, N.; Shi, P.; Li, J.; Wang, Q. Analytical Letters, **2013**, 46, 1991 – 2000. https://research.ebsco.com/linkprocessor/plink?id=d61d091d-68d9-3be7-9aaa-b6084fe8f22e. (accessed Nov. 18, 2024).