Supporting Information for Development of an Alternative Analysis Method to Determine Lead in Eyeliner Cosmetics

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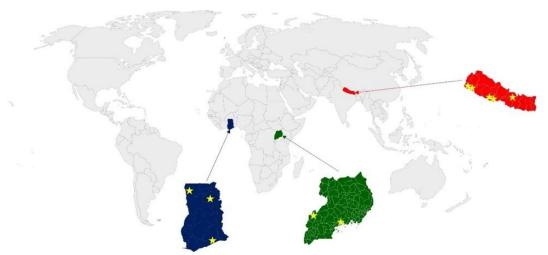


Figure S1: Map of the three countries where eyeliner cosmetic samples were collected. Stars represent the regions in each country where the sample was obtained.

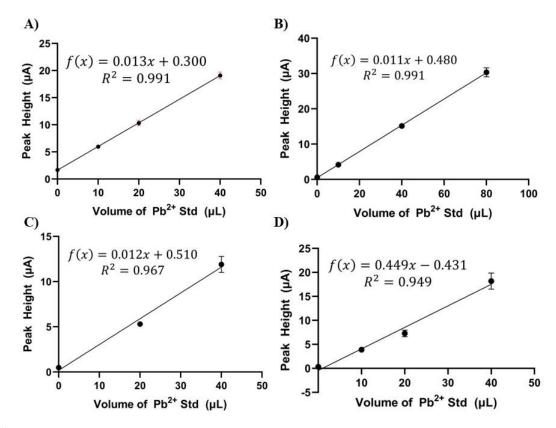


Figure S2: Standard addition plots of A) Sample 1, B) Sample 2, C) Sample 3, and D) Sample 4. Linear regression lines of best fit were used to calculate the x-intercept. The x-intercept was then used to calculate the concentration of the unknown using the concentration and volume of the standard used using **Equation 1**. All data have error bars, but points with small standard deviations are hard to see.

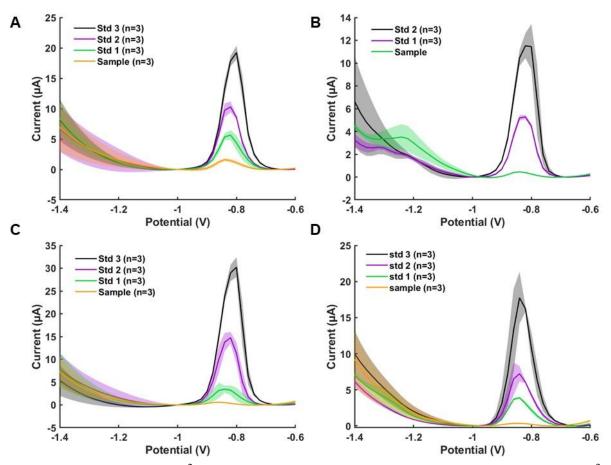


Figure S3: Voltammograms of Pb^{2+} deposition of the lead standards and sample with 2 ppm of Bi^{3+} for **A**) Sample 1, B) Sample 2, **C**) Sample 3, **D**) Sample 4. Analysis was performed in 0.1 M acetate buffer pH 4, 360 s deposition time, -1.4 V deposition potential. Shaded area represents the standard deviation for the voltammograms for n=3.

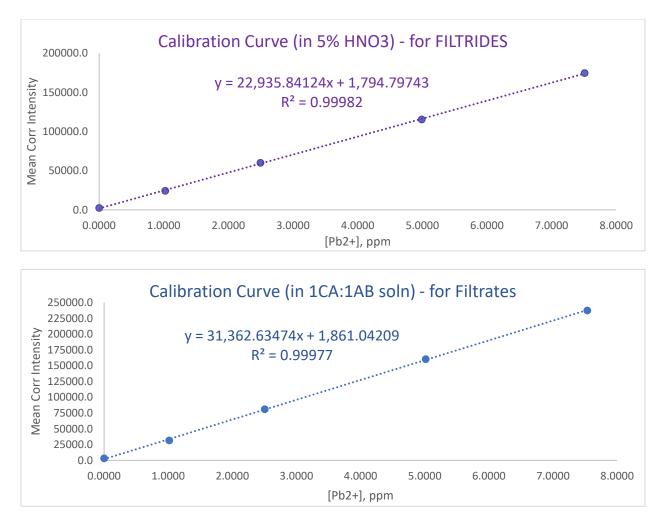


Figure S4. Representative calibration curves for the ICP-OES analysis of Pb^{2+} in the cosmetic samples filtrides (top) and filtrates (bottom). Pb^{2+} concentrations ranged from 0 - 7.5 ppm.

Table S1: Information about the 24 eyeliner cosmetics collected in Nepal, Ghana, and Uganda, including the XRF results, and ICP-OES results. Brands are reported as seen on the label of the cosmetic, and the matrix was determined from the label and physical examination.

| Country | Brand | Matrix | Elemental | ICP-OES |
|-----------|--|--------------|----------------|--|
| Country y | Diana | | Composition | Measured |
| | | | (via XRF) | [Pb ²⁺] _{avg} , ppm |
| NEPAL | S.O.N.A.T.A. Eye Liner Selfish | Liquid | - | 8 ± 2 (n=3) |
| | (KTM-4, Sample 2 ^c) | 1 | | - (- / |
| | S.O.N.A.T.A. Premium Eye Liner | Liquid | - | 2±2 (n=3) |
| | Surma Mamira ^b | Solid/powder | Ca, Pb, Fe, | 1058±10 (n=1) |
| | (S-3, Sample 6^{c} and Sample 1^{d}) | | Zn, Ti, As/Pb | |
| | Perfect Eyeliner | Waxy paste | - | 26±2 (n=1) |
| | Sheetal (SW-2, Sample 4 ^c) | Waxy paste | - | 18±2 (n=3) |
| | Homemade child eyeliner | Dried solid | Ca, Pb, Fe, | 7±2 (n=1) |
| | (SW-3, Sample 3 ^c) | | Zn, Ti, As/Pb | |
| | Ashok | Solid/powder | Ca, Fe, Ni, Zn | 15±1 (n=3) |
| | Eye Improvement Powder | Solid/powder | S, Ca, Fe, Co, | 153±4 (n=1) |
| | | | Cu, Zn | |
| | Surma Mamira ^{a,b} | Solid/powder | Ca, Fe, Mn, | 1939±30 (n=3) |
| | (SW-6, Sample 1 ^c and Sample 2 ^d) | | Zn, Ti, As/Pb, | |
| | | | K | |
| GHANA | Al-Asmad | Solid/powder | Ca, Zn, Cl, | 16±2 (n=3) |
| | | | Fe, K, Mn | |
| | Kohl Al-Sherifain (N-2, Sample 3 ^d) | Solid/powder | Si, S, Zn, Fe, | 136±3 (n=3) |
| | | | Ca | |
| | Lateef Surma | Solid/powder | Zn | 3±2 (n=3) |
| | Mumtaz Delux Kajal Cold (Special Quality) | Waxy paste | - | 2±2 (n=3) |
| | Mumtax Delux Kajal | Waxy paste | - | 19±2 (n=3) |
| | Khojati Surma No. 13 Black | Solid/powder | Zn, Fe | 84±2 (n=3) |
| | Hind Noor Eye Liner | Solid/powder | Ca, Ti, Zn, | 70±3 (n=3) |
| | | | Fe, K | |
| | Hashmi Kohl Aswad ^b | Solid/powder | Pb, Zn | >100,000 |
| | (N-2 child(2), Sample 4 ^d) | | | (n=3) |
| | Hashmi (Natural) Kajal ^b | Waxy paste | - | >500,000 |
| | 1 | | | (n=3) |
| | Hashmi Kohl Aswad ^b | Solid/powder | Pb, Zn | 449±58 (n=3) |
| | Mumtaz Delux Kajal ^b | Waxy paste | - | >100,000 |
| | | XX 7 | | (n=3) |
| | Mumtaz Delux Kajal Cold (Special Quality) | Waxy paste | - | 441±30 (n=3) |
| | Natural rock ^{a,b} (N-2 stone) | Solid/rock | S, Pb | 63±2 (n=5) |
| UGANDA | Starlet Kojal | Waxy paste | - | 35±2 (n=3) |
| | Starlet Kojal | Waxy paste | - | 40±2 (n=3) |

^aSW-6 (commercial eyeliner sample) and N-2 stone (natural eyeliner sample) were analyzed via XRF.

^bDue to the very high concentrations of Pb in these commercial and natural eyeliner cosmetics, these seven samples were not tested via the alternate extraction and electrochemical analysis method.

^dFour samples analyzed via ASV.

^cSix samples from Nepal analyzed via ICP-MS. Due to low sample size, KTM-4, Sample 5 (gel eyeliner) was only analyzed via ICP-MS.

DETAILED MATERIALS AND METHODS FOR ICP-MS:

Sample Preparation: Approximately 50mg of sample was weighed into pre-cleaned 15mL Savillex® Teflon beakers. 4.0mL of double-distilled (DD) concentrated (16N) HNO₃ (Sigma Aldrich) was added to each sample and placed on a hotplate to reflux at 200°C for 48h. Samples were subsequently removed from the hotplate and cooled for 1h. Any sample residue adhered to the sides of the beakers was rinsed with 18 M Ω cm⁻² water. The samples were then placed on the hotplate at 110°C to dryness. 2.0ml of DD 16N HNO₃ was added to the dried samples, and beakers were recapped and placed on the hotplate at 200°C for 48h. Samples were again removed from the hotplate and cooled. Two or three drops of 30% H₂O₂ were added to each sample. Once the reaction subsided, the samples were placed on the hotplate again for 60min. This process of removing the sample to cool and adding H₂O₂ and DD concentrated HNO₃ was repeated until there was no further reaction. Samples were placed on the hotplate at 110°C to evaporate to dryness. Subsequent to this last evaporation cycle, 3mL of DD 16N HNO₃ was added and then diluted to a final volume of ~100mL with 18 M Ω cm⁻² water. Aliquots from the digested solutions were used for both trace elements and isotopic measurements.

ICP-MS Analysis: Trace element concentrations of all solution aliquots were collected on a Nu Instruments AttoM High Resolution (HR) inductively coupled plasma mass spectrometer (ICP-MS). All trace element analyses were conducted in wet plasma mode in medium mass resolution ($M/\Delta M \approx 2500$), and at the start of each analytical session the instrument was tuned and calibrated using a multi element solution (Li, B, Na, Si, Sc, Co, Ga, Y, Rh, In, Ba, Lu, Tl, and U; 1 ng/g). In and Rh were used as an internal standard to monitor and correct for instrument drift and matrix effects. Trace element abundances were calculated based on an external calibration technique.