COMPARISON OF XRF, TXRF, AND ICP-MS METHODS
FOR DETERMINATION OF MERCURY IN FACE CREAM

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Mercury has been used as a skin bleaching agent dates back to the early 1900's, despite its known toxicity and temporary effectiveness. Although the use of mercury in commercial cosmetic products was banned by the EU in 1976 and the U.S. FDA in 1990, this problem persists and these products are still sold in Asia, Mexico, and the Mideast, and can be readily purchased over the internet. Several investigations by various regulatory, media, and watchdog groups identified numerous face cream products containing percent levels of mercury. Clearly, these products represent a significant health risk. The purpose of this study was to develop, evaluate, and compare ICP-MS, XRF, and TXRF methods for accurate quantitation of mercury in 10 different face cream samples.

ICP-MS requires significant sample preparation. For these products, this involved microwave digestion using nitric acid and hydrogen peroxide, and dilution factors on the order of 1,000,000 to bring the solutions into the low ppb calibration range of the ICP-MS instrument. Results showed mercury levels ranging from 0.5 to almost 6%. These same samples were analyzed using a Olympus Innov-X Delta handheld XRF analyzer. Initially, the XRF analyzer was used in soil mode "as is" based on the factory calibration. This gave results that were higher by a factor of two versus ICP-MS, which is not unexpected as this calibration mode is not intended for these types of matrices or when the target element's concentrations are so high that self-absorption is significant. Obviously, authentic standards are needed to obtain more accurate results, and towards this end several different sample preparation and calibration methods were developed and tested. In XRF method 1, standards containing 1-10% mercury were prepared by mixing known masses of mercuric sulfide into a mercury-free face cream matrix. This gave a nonlinear calibration curve and sample concentrations that were 8-42% lower than ICP-MS, most likely due to the differences between the matrices of the samples and standards. In XRF method 2, the samples were diluted by a factor of 100 into an aqueous matrix in an attempt to reduce matrix effects. This required the use of sodium dodecyl sulfate (SDS) to facilitate dissolution of the face cream emulsion. Matrix-matched standards were prepared in the range of 100-1000 ppm. This gave a linear calibration curve and sample concentrations that were 27-188% higher than ICP-MS, which can be attributed to the presence of small flakes of mercury minerals in the diluted samples that settled to the bottom of the XRF sample cup. In XRF method 3, samples and standards were diluted into a Carbomer 940 matrix (which acts as an emulsion to suspend particulate matter), placed in bags, and mixed using a Stomacher® 80 Micro-Biomaster Lab Blender. This gave a linear calibration curve and results that were very close to those from ICP-MS. Lastly, several TXRF methods were developed and used to analyze these same products. Here, the samples were subjected to three different preparation techniques: direct analysis, suspension in surfactant, and microwave digestion with nitric acid and hydrogen peroxide. A small amount of extract from each preparation was mixed with EDTA and Cr internal standard, applied to a quartz disc, and analyzed via TXRF. Direct analysis and suspension techniques gave results similar to ICP-MS with average recoveries of 50-185%. Microwave digestion of the face creams prior to TXRF analysis gave results that were closest to those from ICP-MS with average recoveries of 92%.

If the goal of the analysis is *screening* (i.e., identifying face cream products containing mercury), direct analysis of the products via XRF or TXRF are the fastest and most straightforward methods, as they do not require preparation of standards, involve minimal manipulation of the sample, and give fast turnaround times. If the goal is *accurate quantitation*, this requires homogenization of the sample and/or microwave digestion to obtain more representative and reproducible results. Although XRF and TXRF methods are capable of accurately quantifying mercury down to ppm and ppb levels respectively, they are currently *not acceptable* for regulatory purposes as they are not "approved" methods. However, if these methods indicate mercury levels clearly in excess of the 1 ppm FDA limit for cosmetic products, this begs the question as to why such results are not acceptable as the basis of some regulatory action. The present answer is that until FDA approves either XRF or TXRF methods for these purposes, ICP-MS will remain the method of choice for this and related elemental analysis applications.

This presentation will provide some interesting comparisons between these different techniques, show that XRF or TXRF are ideal methods to screen for these products, and demonstrate that XRF and TXRF methods can provide reliable quantitative results for these products when appropriate sample preparation and calibration procedures are employed.