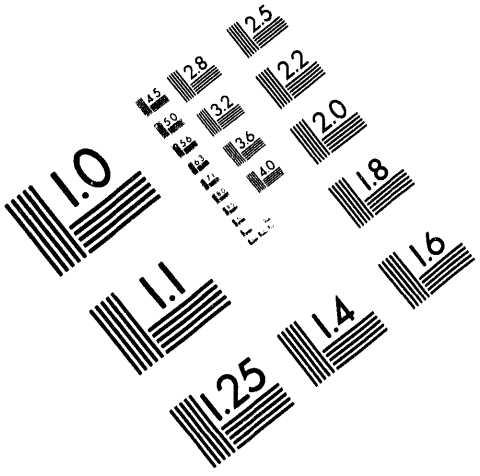

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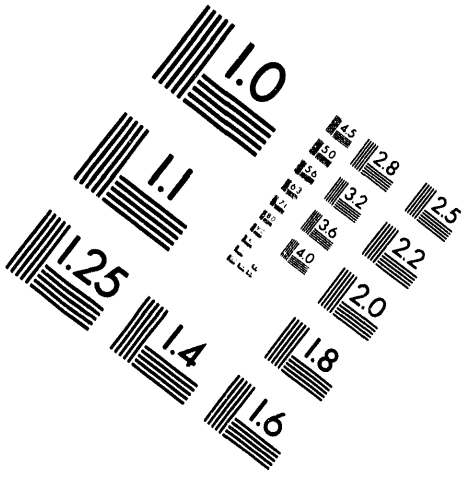

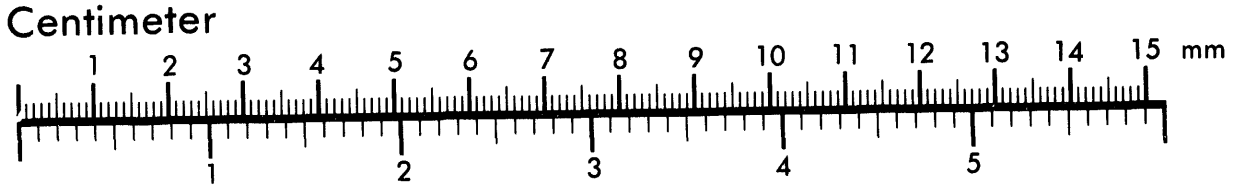


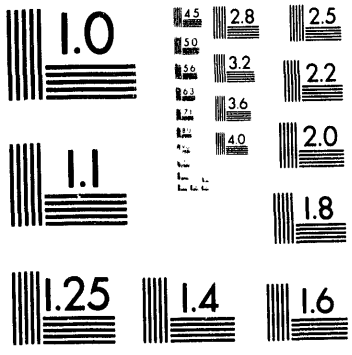

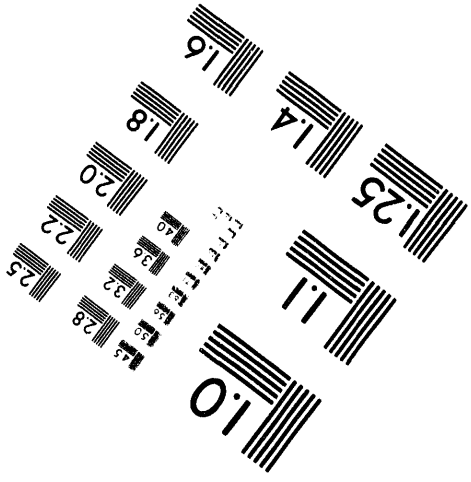

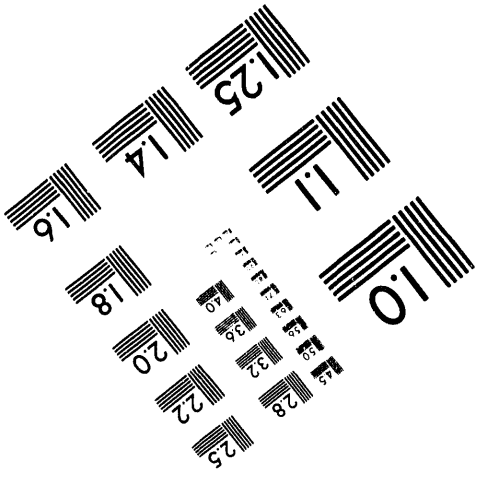

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I. TITLE

*Elemental Impurity Analysis of Mercuric Iodide by ICP/MS**

II. OBJECTIVE

To develop a method to analyze mercuric iodide for elemental contamination using Inductively Coupled Plasma/Mass Spectroscopy (ICP/MS) and to correlate these data with the effectiveness of purification schemes and detector performance.

III. BODY

A. Introduction To Mercuric Iodide

1. Characteristics
2. Synthesis
3. Purification

B. Sample Dissolution Method

C. ICP/MS Instrumentation and Method

IV. RESULTS AND CONCLUSIONS

A. Purification Schemes

B. Gamma Ray and Photocell Detectors



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# ELEMENTAL IMPURITY ANALYSIS OF MERCURIC IODIDE BY ICP/MS[1]

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## ABSTRACT

A method has been developed to analyze mercuric iodide ($HgI_2$) for elemental contamination using Inductively Coupled Plasma/Mass Spectroscopy (ICP/MS). This paper will discuss the ICP/MS method, the effectiveness of purification schemes for removing impurities from $HgI_2$, as well as preliminary correlations between $HgI_2$ detector performance and elemental contamination levels.

## INTRODUCTION

Elemental impurities may be a contributing factor in the performance of $HgI_2$ detectors. Mercuric iodide is synthesized from an aqueous solution of potassium iodide and mercuric chloride. The raw $HgI_2$ goes through a series of purification steps which include vacuum sublimations, melts, resolidification, and closed system sublimations. Zone refining is also being used to purify starting chemicals and as a final purification step for the $HgI_2$. The purified $HgI_2$ is then grown into a single crystal by physical vapor transport. The crystals are cut into slices and they are fabricated into room temperature radiation detectors and photocells. Crystals that produce good resolution gamma detectors do not necessarily make good resolution photocells or x-ray detectors. Many factors other than elemental impurities may contribute to these differences in performance. A method has been developed to utilize ICP/MS to determine elemental impurities.

ICP/MS analysis require the dissolution of samples. Mercuric iodide is a difficult compound to analyze for trace quantities of elemental impurities for several reasons. The solvent must dissolve all impurities in the sample and it must be ultrapure. Sample size can be very limited, on the order of one gram or less. The major matrix components, mercury, iodine, and acid reagents, can obscure and interfere with the detection of the low levels of some elements present in the samples.

There are two methods employed to dissolve $HgI_2$. The first is to dissolve the solid $HgI_2$ crystal in an aqueous solution of 1% KI. This technique dissolves the $HgI_2$ matrix but is probably not rigorous enough to dissolve particulate contaminants within the crystal structure. The second method is to use aqua regia as the solvent. This paper discusses this analytical method as applied to purification methods for $HgI_2$ and KI.

## EXPERIMENTAL

### Sample Dissolution Method

Dissolution of $HgI_2$ in high-purity (Seastar) nitric acid was not successful even with microwave digestion. Aqua regia (three parts HCl and one part $HNO_3$) is known to readily dissolve $HgI_2$. However, for ICP/MS analysis, it is desirable to avoid high concentrations of chloride because the formation of metal chlorides and oxychlorides interferes with the analysis (e.g., $^{35}Cl^{16}O$ interferes with $^{51}V$). Therefore, the minimum

amount of HCl required to effect complete dissolution of $HgI_2$ was studied. Experiments showed that 0.5 grams of $HgI_2$ treated with 0.1 ml HCl + 5.0 ml $HNO_3$ + 30 minutes of microwave treatment at 50% power left a solid, black deposit with a metallic luster, presumably $I_2(s)$, on the walls of the Teflon digestion bomb. The addition of 0.5 ml HCl and further heating causes the solid to disappear and a white crystalline precipitate (thought to be $I_2O_5$) is observed in the concentrated nitric acid. The reaction is nearly stoichiometric. Half a gram of $HgI_2$, containing 2.2 mmoles of iodine, requires 0.5 ml HCl to provide a slight excess of NOCl (the oxidizing species in aqua regia) to take the reaction to completion. Samples prepared in this manner show elevated $^{51}V$ signals, possibly due to the formation of $^{35}Cl^{16}O$. The addition of 1.0 ml $HNO_3$ to the crystalline $HgNO_3$ product and two subsequent reevaporation steps show a marked reduction in the $^{51}V$ signal.

Therefore, the following procedure for the dissolution of $HgI_2$ and KI is used:

1. Weigh out 0.5 grams of $HgI_2$ into a Teflon microwave dissolution bomb.
2. Add 5.0 ml Seastar nitric acid.
3. Add 0.5 ml Seastar hydrochloric acid
4. Microwave at 50% power for 15 minutes. If dissolving single crystals rather than a powder, more time and more HCl may be required. If $I_2(s)$ is still present on the walls, add HCl in 0.1 ml increments and microwave for an additional 15 minutes.
5. Transfer contents to a Teflon beaker with deionized $H_2O$.
6. Heat on a hot plate evaporate to dryness and the appearance of white crystalline $Hg(NO_3)_2$.
7. Dissolve $Hg(NO_3)_2$ in 1 ml of Seastar nitric acid and wash walls with deionized water.
8. Evaporate to dryness and reappearance of $Hg(NO_3)_2$.
9. Dissolve in 1 ml of Seastar nitric acid and a little deionized water.
10. Transfer solution to clean polyethylene sample bottle. If desired, add internal standard concentration spike of 0.5 ml of 10 ppm indium (In). Dilute to 100 ml with deionized water.

## ICP/MS Instrumentation and Methods

A Finnigan MAT (San Jose, CA) SOLA ICP/MS (formerly Turner Scientific) is used for elemental analysis. Table I contains the typical instrument parameters used for trace elemental analysis of up to 1% $HgI_2$ solutions.

**Table I. Typical ICP-MS Instrument Parameters**

| | |
|---|---|
| Nebulizer | Standard Meinhard |
| Torch | Standard size |
| Argon coolant gas flow rate | 15 L/min. |
| Argon auxiliary gas flow rate | 0.75 L/min. |
| Nebulizer gas flow rate | 0.85 L/min. |
| Sample flow rate | 1 ml/min. |
| Sampling cone | Nickel - 1 mm orifice diameter |
| Skimmer cone | Nickel - 0.8 mm orifice diameter |
| Detector mode | Ion counting electron multiplier |
| Scan parameters | 16 channels/u<br>5 passes/scan<br>5 scans/analysis |

The instrument is set to analyze for only one isotope per element of interest. Particular isotopes are avoided due to well known spectral interferences, as shown in Table II. Spectral studies show no interferences above 10 parts per trillion in the molybdenum mass region due to $Hg^{+2}$. Furthermore, studies using standard solutions of Na, Co, In, Lu, Pb and U in different concentrations of $HgI_2$, show no significant ionization effects from salt loadings of up to 1% $HgI_2$.

**Table II. Known ICP/MS Spectral Interferences for $HgI_2$ Analyses**

| Mass | Isotope | Interference |
|---|---|---|
| 28 | $^{28}Si$ | $N_2^+$ |
| 29 | $^{29}Si$ | $N_2H^+$ |
| 30 | $^{30}Si$ | $NO^+$ |
| 51 | $^{51}V$ | $^{35}Cl^{16}O^+$ |
| 54 | $^{54}Fe$ | $ArN^+$ |
| 56 | $^{56}Fe$ | $ArO^+$ |
| 63.5 | $^{63}Cu$ | $^{129}I^{+2}$ |
| 67 | $^{67}Zn$ | $^{35}ClO_2^+$ |
| 69 | $^{69}Ga$ | $^{37}ClO_2^+$ |
| 78 | $^{78}Se$ | $^{38}Ar^{40}Ar$ |
| 142 | $^{142}Nd$ | Tail of $^{127}I^{16}O^+$ |
| 165 | $^{165}Ho$ | Tail of $^{39}K^{127}I^+$ |
| 166 | $^{166}Er$ | $^{39}K^{127}I^+$ |
| 236-244 | $^{235}U$, $^{238}U$ | $HgAr^+$ |

For regular crystal and salt comparisons a semiquantitative analytical method is used. In this technique 61 elements are selected for analysis as shown in Table III. All of the samples and reagent blanks are spiked with 50 ppb In, which serves as an internal standard. The relative sensitivity factors (used for calculation of concentrations) for all of the elements are set to unity. This allows for rigorous intercomparison of the relative concentrations of the elements, from sample to sample, without the need for complete standardization for all of the elements.

**Table III. Selected Elements for Analysis**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Li | Ti | Ga | Nb | Sb | Sm | Lu | Tl |
| Be | V | Ge | Mo | Te | Eu | Hf | Pb |
| B | Cr | As | Ru | Cs | Gd | Ta | Bi |
| Na | Mn | Se | Rh | Ba | Tb | W | Th |
| Mg | Co | Rb | Pd | La | Dy | Re | U |
| Al | Ni | Sr | Ag | Ce | Er | Os | |
| Ca | Cu | Y | Cd | Pr | Tm | Ir | |
| Sc | Zn | Zr | Sn | Nd | Yb | Pt | |

## Sample Selection

The first samples selected for analysis were taken from all of the purification steps of EG&G synthesis $HgI_2$ lot #124. These analyses assess the effectiveness of the purification steps in removing elemental contamination from the $HgI_2$. The capability of zone refining as an additional purification step for both $HgI_2$ and KI was also evaluated. Samples were selected from the front, center, and rear sections of each zone-refined sample.

## RESULTS

### Purification Steps

The analysis of the raw synthesized $HgI_2$ and the six subsequent purification steps show that for most elements the concentrations change by less than 50% over the entire sequence of steps. An example is shown in Figure 1. Noted exceptions are Co and Ni which are found to be lower in the raw $HgI_2$, as shown in Figure 2. The decontamination factor is defined as the measured concentration divided by the concentration measured in the raw $HgI_2$.

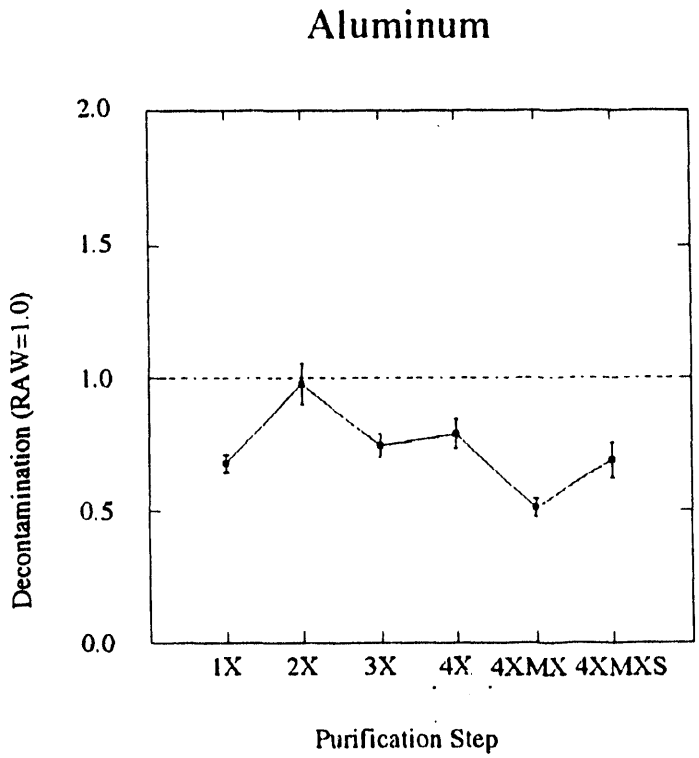


**Figure 1. Effect of Purification Steps on the Concentration of Al in $HgI_2$.**

### Zone-refined $HgI_2$

The levels of elemental contamination in the zone-refined $HgI_2$ were higher in the center section than in either the front or rear sections for most elements. However, the rear section of the tube contains the highest levels of impurity contamination for Mg, Ca, Sc, Ti, Mn, Fe, Cu, Zn, and Sb. The zone refiner normally sweeps impurities from the rear to the front.

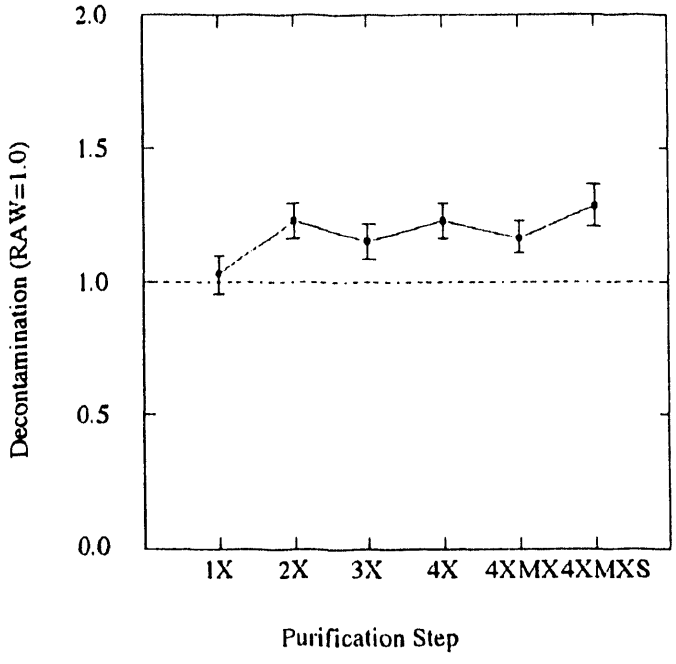


**Figure 2. Effect of Purification Steps on the Concentration of Ni in $HgI_2$.**

## Zone-Refined KI

The front section of the KI zone-refined tube contains the highest concentration of impurity contamination for most elements. The only exceptions are Cr, Mn, Ce, and Pb. The total elemental contamination for the front section is approximately 480 ppm, while the center and rear sections each contain 15 ppm total impurities.

## DISCUSSION

The $HgI_2$ purification steps do remove some impurities from the raw synthesized $HgI_2$. The extent of removal, approximately 50% reduction in elemental contamination levels, is not as dramatic as expected. The results from the zone-refined $HgI_2$ samples are puzzling because zone refine theory would suggest that impurities should be moved to one end of the tube, and not concentrated in the center section of the tube. On the other hand, the zone-refined KI results follow the expected trends, with impurities being moved to the front section of the zone refining tube.

## FUTURE DIRECTIONS

Samples from $HgI_2$ crystals and detectors are being prepared and analyzed to determine if correlations can be made between detector performance and elemental impurity concentrations.

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