

Automated Determination of PPQ Levels of Thorium in High Purity Copper

Using the ESI TRUFAST System and ICPMS Detection

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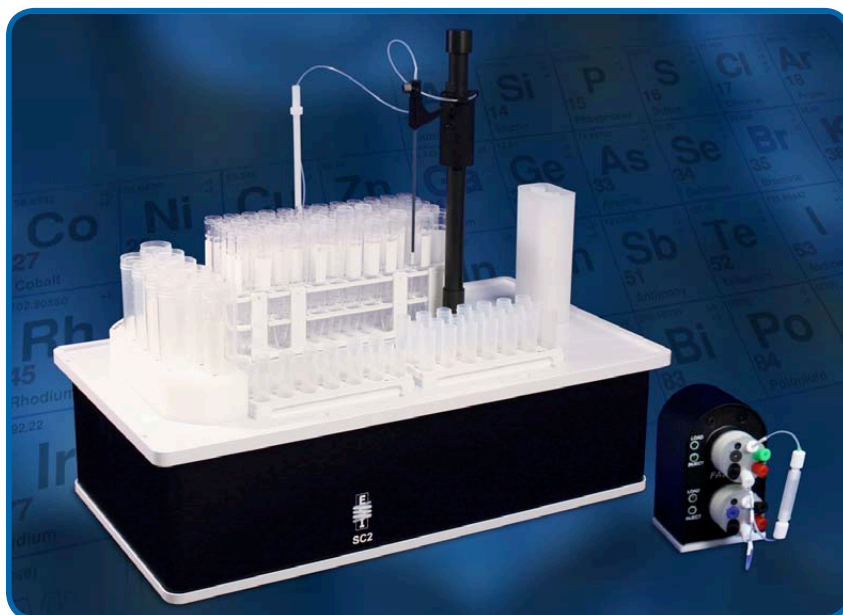
Introduction

Alpha decay from semiconductor device package materials is a root cause of “soft errors” in microprocessors and storage devices. Reducing the concentration of Th ($t_{1/2} = 1.4 \times 10^{10}$ years) and other alpha emitters in copper package material will yield a corresponding reduction in alpha decay events and soft errors. Improved analytical capability allowing the detection of single digit ppq concentrations of Th in Cu would facilitate process improvements and ensure product quality.

This note describes an automated in-line system which uses a PFA column packed with TEVA[®] Resin to retain Th from a solution of 1% Cu and 8% HNO₃ while the Cu matrix passes through to waste. The pre-concentrated Th is eluted from the column using high purity HCl and detected by ICPMS. Thorium calibrations are linear over more than 4 orders of magnitude with washout factors (sample-to-sample) better than 1000x. Long-term stability (60 samples) was better than 2% RSD at 100 ppt Th. The Th detection limit (3σ) is less than 10 ppq and could be improved further by reducing the procedural blank. Cu samples were prepared by dissolution in high purity HNO₃ and brought to a final concentration of 1% Cu in 8% HNO₃ in a PFA Teflon vessel. ICPMS standards are prepared in 8% HNO₃ at concentrations ranging from 50 ppq to 1 ppb Cu.

Matrix effects of high levels of Cu (1% solutions) cause significant signal suppression in ICPMS, so matrix removal is essential to achieve the best detection limits. Simple dilution of the sample matrix is not possible as Th is already close to the detection limit of ICPMS systems. It is therefore necessary to remove the Cu matrix while maintaining or increasing the Th signal.

The TRUFAST uses the PFA column packed with TEVA Resin to concentrate Th from a solution of Cu dissolved in HNO₃, allowing for accurate measurement at low ppq levels. The TRUFAST system diagram is shown below.



SC-2 DX TRUFAST Preconcentration and Matrix Removal System

Experimental

Instrumentation, Sample Introduction, and ICPMS Parameters

- TRUFAST Sample Introduction System
- Thermo Scientific ELEMENT2 ICPMS
- CF-TEVA 50 μ L resin column
- Eluent Flow Rate: 200 μ L/min
- Sample volume: 4 mL

Table 1. ICPMS Conditions

Parameter	Value
Rf Power	1400 Watts
Nebulizer Gas Flow	0.7 L/min
Plasma Gas Flow	16 L/min
Auxiliary Gas Flow	0.9 L/min
Additional Gas Flow	0.15 L/min

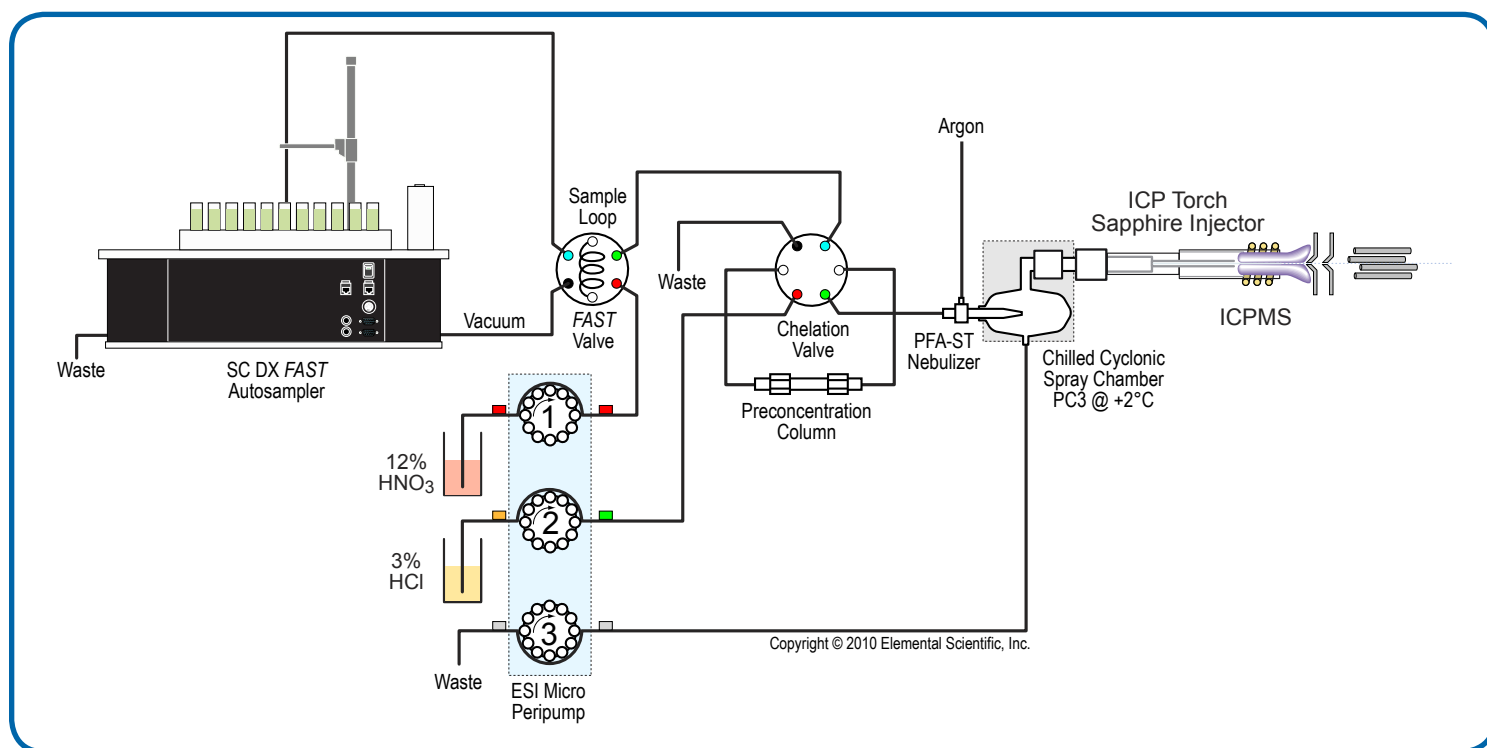


Figure 1. System diagram for determination of Th and Cu by pre-concentration and matrix removal

Procedure

The TRUFAST system uses two high purity valves to take up an aliquot of sample, concentrate it on a PFA column packed with TEVA Resin, and elute the Th into a PFA nebulizer attached to an ICPMS spray chamber. Standards (8% HNO₃) and samples (1% Cu and 8% HNO₃) are vacuum loaded into a 4 mL sample loop on the FAST valve. The FAST valve switches to inject the sample into the column. The TEVA Resin retains the Th in the sample while the Cu matrix, which is not retained by the resin, is washed out of the column for 3 minutes with 12% HNO₃.

After the Cu matrix has been removed from the column, the chelation valve is switched allowing 3% HCl to pass through the column to elute the Th as a transient peak. The sensitivity of this peak and the concentration of Th in the samples can be measured and calculated via the ICPMS software. Once the Th has been eluted from the column, the chelation valve is switched to recondition the column prior to the next analysis. The total run time is 11 minutes sample-to-sample.

Elution

An elution curve can be obtained in less than 60 seconds. The levels at sub-ppt show strong elution peaks, as shown in Figure 2.

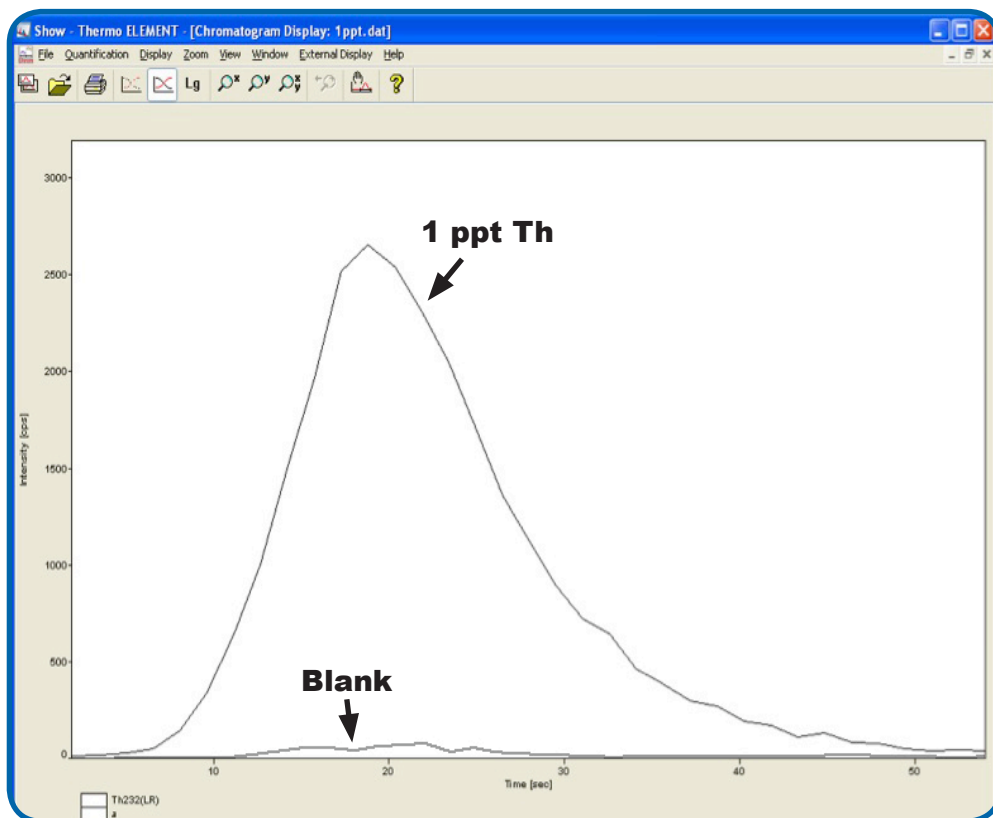


Figure 2. Overlaid elution profiles of the procedural blank and 1 ppt Th²³².

Calibration

Figure 3 shows Th²³² calibration generated in external standards from 0 ppt to 1000 ppt, demonstrating excellent linearity across four orders of magnitude. However, when generating calibration curves it is best to restrict data point to within an order of magnitude of expected results. This prevents error in the high standards, such as 1000 ppt, from affecting the measurement of lower traces, such as 1 ppt.

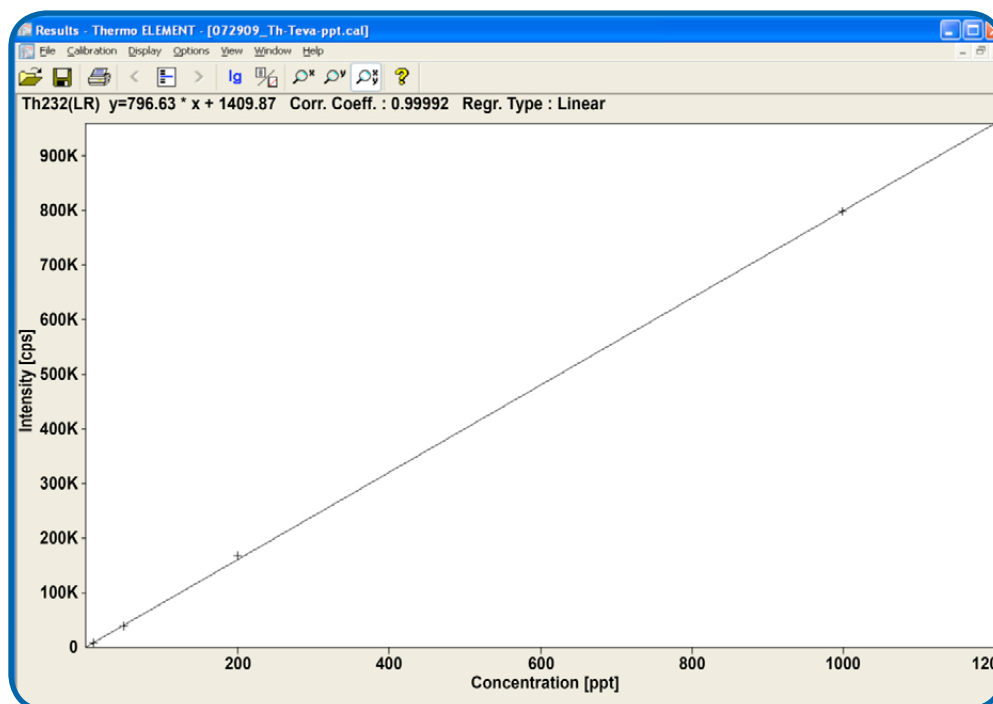


Figure 3. Calibration curve for Th in Cu up to 1000 ppt.

Figure 4 shows a separate calibration of Th^{232} from 0 ppt to 1 ppt, with measurements taken at 0.05 ppt, 0.1 ppt, 0.5 ppt, and 1 ppt.

The average 10 ppt Th spike recovery for 3 injections in a 1% Cu matrix was 10.1 ppt or 101%. The LOD (3σ) for Th in 1% Cu was 8 ppq.

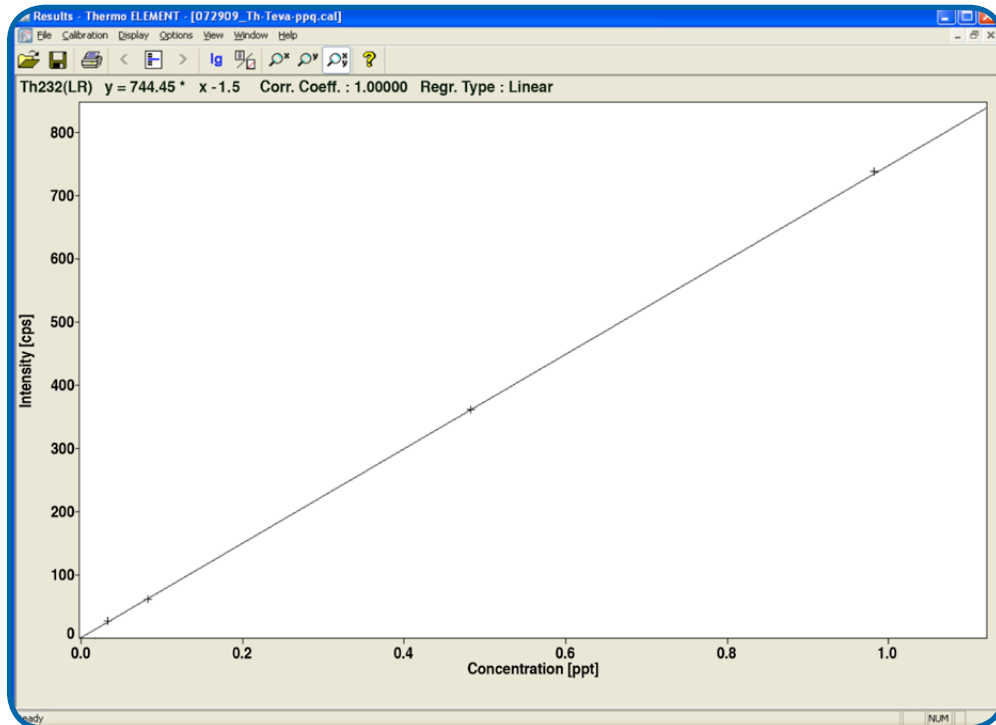


Figure 4. Calibration curve for Th in Cu up to 1 ppt.

FAST Washout

After a 1 ppb sample is analyzed, the thorium washout is better than 1000x in the first blank. The second blank shows 4000x washout, while the third blank shows 8000x washout. The TRUFAST system may be configured to perform additional wash steps if triggered from the instrument QC function. If sample concentration is more than 1000x higher than the desired detection limit, then an extra rinsing step should be employed.

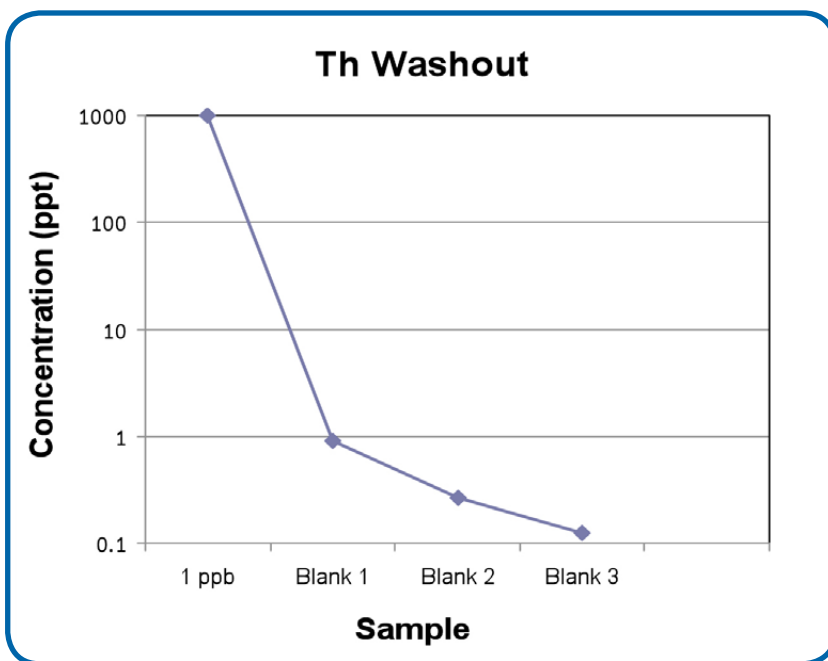


Figure 5. Washout analysis of 3 blanks after a 1ppb sample

Long-Term Stability

Long-term stability was evaluated repeatedly by measuring 100 ppt Th. Three bottles spiked with 100 ppt Th were each analyzed 20 times preceded and followed by blanks. The retention of Th on the column remains constant even after running many samples over a long period of time.

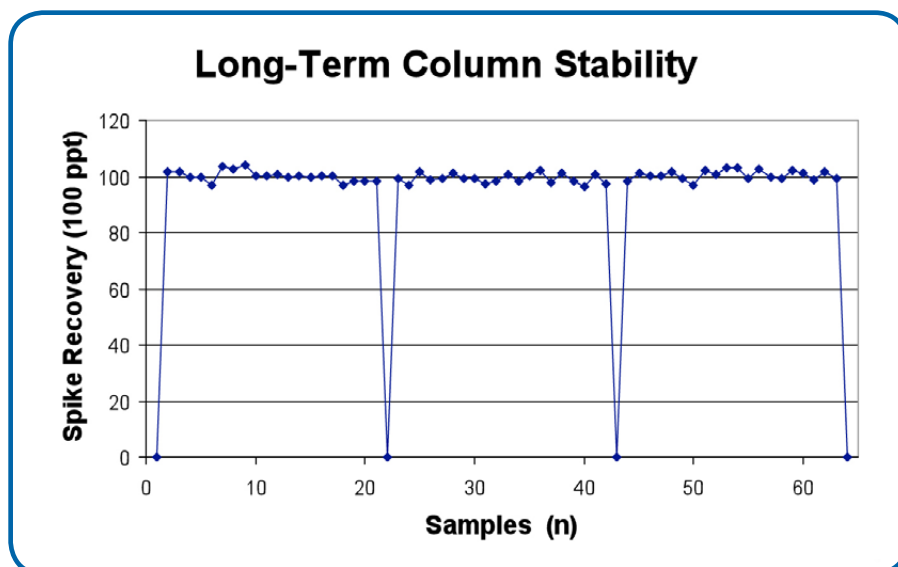


Figure 6. 60 replicate determinations of 100 ppt Th in 1% Cu from three 100 mL sample bottles.

Conclusion

With its automated and versatile sample uptake and introduction capabilities, the TRUFAST system offers easy and efficient determination of low ppq levels of Th in high purity Cu. The TRUFAST system reduces sample prep time while achieving low ppq level detection limits. The long-term stability and washout characteristics of the column provide economical and time-saving advantages over systems with single use columns.

References

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- 2) C. Cabral Jr., K.P. Rodbell and M.S. Gordon, Alpha particle mitigation strategies to reduce chip soft error upsets. J. Appl. Phys. 101, 014902 (2007).
- 3) M. Fukuda, Y. Hayashibe and Y. Sayama, Determination of nickel, cobalt, copper, thorium and uranium in high-purity zinc metal by ICP-MS with online matrix separation. Anal. Sci. Vol. 11, 13-16, (1995)