# Deconvolution of Isobaric Interference in ICP-MS by Peak Shape Calibration Technology

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# Overview

A new deconvulotion method based on mass spectral peak shape calibration was developed for mixture analysis of overlapped ICP-MS data

On a unit mass resolution quadrupole ICP-MS instrument, As at 1 and 10 ppt with the interference ArCl at a various concentration levels were accurately quantified through the deconvulction by MassWorks.

# Introduction

Much of ICP-MS development in the last twenty years has centered around collision cells for the physical removal of interferences through reaction chemistry. While guite useful and effective in real world applications, the use of collision cells and the associated chemistry does compromise the analytical sensitivity. In addition, there are interferences that are difficult to remove through chemical reactions even after extensive method development. In this paper, we report a new approach to quantify analyte of interest at presence of interference. Based on peak shape calibration technology, this approach has proved to be very effective to deconvolute overlapped ion signals such as the mixtures of 14C/12C in drug metabolism studies, molecular ions and their fragments (M-H) in ELGC/MS, the parent ions and their oxidized products. Since most of the interference occurred in ICP-MS is known and can be expressed by a chemical formula, the deconvolution can be readily implemented through the mixture search by MassWorks. We will demonstrate the deconvolution with the analysis of the mixtures of As and the interference ArCl at different concentration levels

# Methods

Data Acquisition: All data were acquired in survey mode with a mass range from 0 to 260. The experiments were designed to focus on the studies of As and its isobaric interference ArCL A total of three datasets were collected including pure As standards at 1, 10, and 100 ppt; As standard at 1 ppt with addition of solution containing [CI] at 10, 100, 1000, 2000, 5000, and 10000 ppm; and As standard at 10 ppt pus [CI] at 100, 1000, 2000, 5000, and 10000 ppm. The raw data of ICP-MS were exported into text data format for MassWorks to process.

>MassWorks processing: All the data were calibrated through a new mass spectral calibration that not only calibrates the m/z axis but, more importantly, calibrates the mass spectral peak shape. With the theoretical mass spectral responses for the ion of interest and possible interference ions known exactly, a multiple linear regression can be applied to any measured mass spectral response after the above calibration to arrive at the relative concentrations of these ions including both the unknown and the interference.

Quantitation of As: A quantitation calibration curve was generated by As standards at 1, 10, and 100 ppt. Through the calibration, deconvoluted As at 1 and 10 ppt levels spiked with [C1] interference were quantified.



For this application, As as a standard was used for both mass and peak shape calibration to enable highly accurate isotope pattern matching for mixture analysis by deconvolution.

#### Fig 1. Mass and Peak Shape Calibration with As Standard at 100 ppt



data files to perform spectral deconvulotion to obtain quantitative information of As at the presence of ArCI interference by CLIPS search. To take ArCI as an experimentally designed only interference into account, the formula of ArCI needed to be input for the deconvulotion as shown in Fig 2. Since the peak shape of the spectra was calibrated to known mathematic function (Fig 3a) through the calibration, the best match between theoretically composite As and ArCI spectra and experimental spectra has been achieved with spectral accuracy of over 98%. This high spectral accuracy indeed confirmed the overlapped spectra were due to the signals from only As and ArCl. Their relative contribution to the total signal is accurately calculated by spectral deconvolution in a sample with 10 ppt spiked with



Fig 3. Raw, Calibrated, and Calculated Spectra of m/z 75



5000 ppm [Cl<sup>-</sup>] as shown in Fig 4a. The calculated As concentration through deconvolution is 9.68 ppt (Table 1) which is consistent with expected value 10.0 ppt.

The spectral deconvolution can also help troubleshoot some experimental errors. In Fig. 4b, the sample having also 40 ppt but spiked with 10000 ppm [CI] shows that the total signal is dominated by ArCl and has much less contribution from As compared with that in Fig. 4a. This suggests the experimental errors in this sample were related to any preparation procedures of As unless some unusual



#### Table 1. Quantitation Results of As by Spectral Deconvolution

Spectral Deconvolution					
Conc. of As	Reponse of As	Conc. of As	Conc. of As	StDev	Notes
Prepared	Calculated	Calculated	Averaged		
blank	0	0.10			
1	3.92	1.06			Calibration samples
10	40.54	9.94			
100	411.76	100.01			
1	4.93	1.30			
1	3.91	1.05			
1	-2.03	-0.39			
1	7.02	1.81			
1	6.16	1.60			
1	7.25	1.86	1.21	0.84	
10	39.30	9.64			
10	41.55	10.19			
10	37.15	9.12			
10	39.92	9.79	9.68	0.44	
10	14.48	3.62			outlier

interference was introduced during preparation to generate additional signal at m/z 77 such that the spectral deconvolution needs to maintain the isotope profile of ArCI and result in less As to be accounted for.

The deconvolution results for all the samples are shown in the column of "Response of As, calculated" in Table 1. According to quantitation calibration by the pure standards (data not shown), all the concentrations of As were calculated and summarized in the table. We found that there were significant variations on the concentration for the AS samples prepared at 1 ppt level with standard deviation of 0.84. The large errors were likely due to poor signal to noise ratio. On the other hand, much better results were found for the As samples at 10 ppt level with much smaller standard deviation than that at 1 ppt level.

#### Fig 5. Calculated and Prepared Conc. of As (ppt)



## Conclusions

>With peak shape calibration performed with As standard, symmetrical and mathematical well defined peak shape can be obtained for all ICP-MS spectra for the mixtures of As spiked with [ Cl<sup>-</sup>] and allows accurate spectral deconvolution and quantitation of the mixtures.

Low concentration samples at 1 ppt levels showed significant signal variation due to their poor S/N ratio. Their S/N ratio can be improved by decreasing scan range from 0-260 to 70-80 for As related deconvolution.

Current version of MassWorks can perform three components mixture analysis. In a future release, multiple components, virtually unlimited components can be performed with the spectral deconvulotion.

## References

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