Novel Low Volume Autosampler for ICP-MS

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Introduction & Objectives

The need for small volume aliquot injection is not new. As scientific investigation continues to look closer at smaller objectives new tools are required that are suitable to these small subjects. As these tools are developed new application areas where ICP-MS had previously not been utilized can be explored.

In this study a flow injection autosampler is presented that was developed with small aliquots in mind. This system is similar to that found in liquid chromatography, however each of the wetted parts are non-metallic as to keep the ICP-MS background very low. Additionally, this system does not waste sample during the injection, the volume is taken up by the needle, then the needle is injected into the valve. The injected sample is then pushed into the nebulizer by use of a secondary syringe pump. The syringe pump allows for smoother flow compared with the peristaltic pump.

In order to show the application of such an autosampler, small volumes of isolated protein were ran for this study. The amphibian *Xenopus Laevis*, the South African Clawed Frog, was the subject of this study. The broader scope of the scientific investigation is to learn the role of zinc for the ability of Cdc25C to activate MPF/cdk1. By creating the tools and methods for small aliquot sampling additional studies of elements at lower concentrations may be possible, and using different organisms.

Figure 1: *Xenopus Laevis*, South African Clawed Frog (photo by Brian Gratwicke)

This particular species is used in toxicology testing for determining teratogenicity. The element of interest in this study is Zinc. Zinc is an essential micronutrient for the growth and development of multicellular organisms, Zn deficiencies lead to growth retardation and congenital malformations (Vallee & Falchuk, 1993). In this study isolated protein from *Xenopus Laevis* are studied for their zinc content using a Low Volume autosampler.

Materials & Methods

Protein samples were isolated and collected using previously described methods (Sun, et. al, 2007). Samples of varying volumes between 100 µL and 200 µL were thawed and subjected to sample pre-treatment. An aliquot of 50 µL was digested with 5% H_2O_2 and 50% HNO_3, then diluted with milli-q water with Yttrium serving as an internal standard. NIST 927 was ran alongside to served as a matrix matched standard. This particular standard, Protein Serum Albumin is not certified for zinc, however was ran to determine its Zinc content and any other spectral interferences. Additionally NIST 927 served as a matrix spike sample. Two other protein samples were also used as matrix spike samples. The spike was set to 500 µg/L.

Figure 2: Low Volume Autosampler

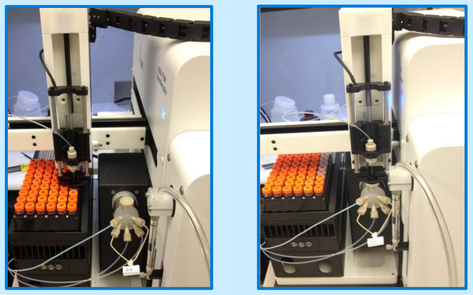

Figure 3: Sample aliquot (left) and sample injection (right)

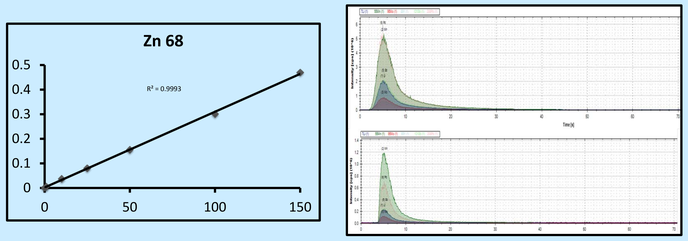

Figure 4: Zn regression plot (left), 5 µL injection (top right) 0.5 µL Injection (bottom right)

Results & Discussion

Table 1: Injection Repeatability with 5 µL loop installed

Repeatability (RSDs)					
Injection	**Li**	**Mn**	**Mo**	**Sb**	**Pb**
5 µL Full	**1.043**	**1.704**	**0.765**	**1.852**	**1.518**
5 µL Partial	**1.7**	**1.308**	**1.219**	**1.593**	**2.416**

Table 2: Injection Repeatability with 20 µL loop installed

Repeatability (RSDs)					
Injection	**Li**	**Mn**	**Mo**	**Sb**	**Pb**
20 µL Full	**1.057**	**0.779**	**0.623**	**0.922**	**1.173**
20 µL Partial	**1.133**	**0.980**	**1.054**	**1.594**	**2.374**

Table 3: Zinc results from Xenopus Laevis

Isolated Protein from Xenopus Laevis		
Sample	**Zinc µg/L**	**% Recovery**
DCT	**560.8**	
HG2A	**516.8**	
C457A	**646.1**	
C507A	**508.5**	
C513A	**374.8**	
C513A Spike	**828.1**	**94.65**
AHHA	**383.3**	
AHHA Spike	**850.3**	**96.26**
NIST 927	**108.3**	
NIST 927 Spike	**574.2**	**94.39**

Conclusions

This suite of samples display the utility of the autosampler and its specific advantages over traditional sample introduction for small samples. No sample is wasted which would happen using a pull through sample aliquot.

The concentration of zinc in these samples was at a level that is easily detected by quadrupole ICP-MS. The autosampler allows users to investigate small sized samples and future studies will look at small samples with elements at trace levels.

References

Vallee BL, Falchuk KH. 1993. The biochemical basis of zinc physiology. Physiol Rev 73:79-118

Sun L, Chai Y, Hannigan R, Bhogaraju V, Machaca K, 2007, Zinc regualates the ability of Cdc25C to activate MPF/cdk1