

## **Effect of sodium and carbon on analytical determination of ultratrace metals in bio specimens by ICP-MS**

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Human blood is composed of blood cells suspended in blood plasma. The plasma is a complex mixture of 95% water and 5% suspended or dissolved biomolecules, nutrients, physiological waste products and inorganic ions. The remaining inorganic components constitute about 1% of the total mass of plasma. Precise and accurate determination of trace elements in blood, plasma or serum is essential for human biomonitoring studies, which allows us to compare concentration levels among different study populations and correlate health effects with exposures to various elements.

A sensitive and high-throughput method was developed for ultra-trace analyses of Mn, As, Cd, W, Hg, Pb and U in blood plasma specimens using inductively coupled plasma mass spectrometry (ICP-MS) equipped with a He mode collision cell. Although only analysis of human plasma for trace metal content is discussed, the method was successfully used for blood analysis as well. Calibration standards were prepared in basic solution with NaCl and n-butanol (present in the diluent) as Na and C sources, respectively. The remaining components of the diluent were, NH<sub>4</sub>OH, H<sub>4</sub>EDTA, Triton X-100 and internal standards (Ga, Rh, Re and Ir). Both calibration standards and plasma specimens were diluted 1:10 and directly injected, using an integrated sample introduction system (ISIS), to the ICP-MS bypassing the time consuming and contamination prone chemical/heat digestion steps used elsewhere. The addition of 2% n-butanol to the calibration standards caused a substantial signal enhancement - as much as 450% for As and 120-130% for the other elements - due to the charge transfer from carbon ions (C<sup>+</sup>) to analytes in the instrument plasma. Further increase in n-butanol concentration steadily decreased elemental signal intensities in a very similar way as the addition of NaCl.

The relationships between signal intensities of C<sup>+</sup>, Na<sup>+</sup> and Cl<sup>+</sup> and the concentration of n-butanol in a mixed solution of n-butanol and NaCl is shown in Fig 1. When NaCl was present in the solution, even the Na<sup>+</sup> signal intensity was noticeably decreased with increasing C<sup>+</sup> concentration due to a much higher total concentration of C and C<sup>+</sup> than Na and Na<sup>+</sup> in the instrument plasma. Simultaneously, C<sup>+</sup> signal intensity was leveling, indicating strong ionic interactions. Both C<sup>+</sup> and Na<sup>+</sup> signal intensities in the instrument plasma were at a similar level and their suppressing effect on analytes and internal standards seemed to be interchangeable. Therefore, a thermodynamic approach where one or more ions at higher concentration can influence ionization of other elements present in the instrument plasma at much lower concentrations, which would describe the observed phenomena.

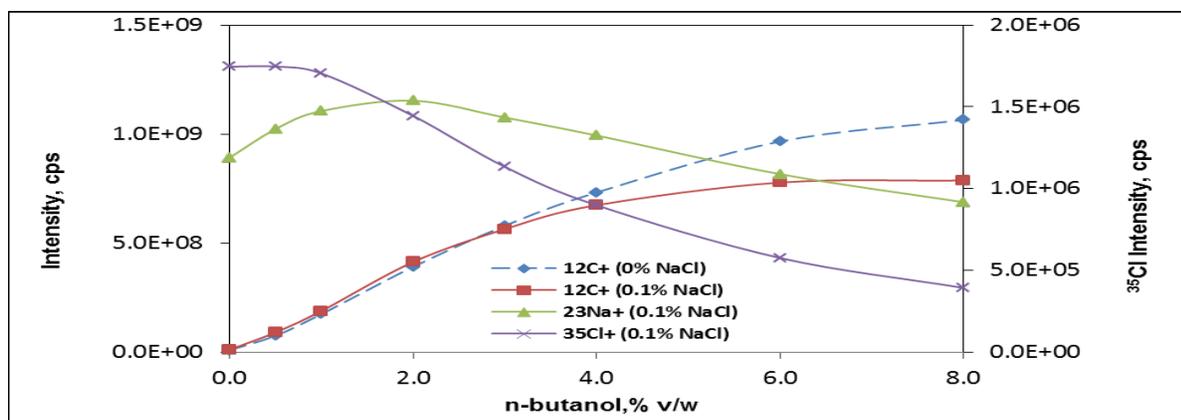


Fig.1 Effect of n-butanol concentration on signal intensities of carbon, sodium and chloride species.

These findings were helpful to determine the optimal concentration of 1% NaCl in the intermediate calibration standards and 4% of n-butanol in the diluent to matrix-match the suppressing effect of inorganic and bio-organic components of plasma specimens (Fig.2).

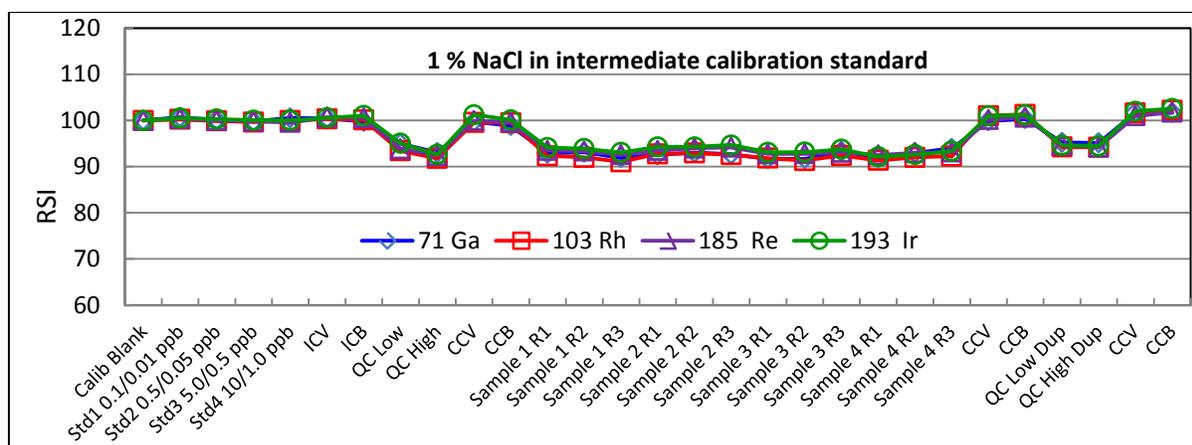


Fig. 2. Relative standard intensities (RSI) during analytical run with 1% NaCl concentrations in intermediate calibration standards. The RSI are ratios of elemental signal intensities in a sample and the calibration blank.

The addition of carbon is necessary to maximize elemental signal enhancement of the analytes and the internal standards in calibration standards and specimen solutions, while Na<sup>+</sup> provides a matrix-match effect with the inorganic easy ionized elements present in the bio specimens. The higher suppression of the signal intensities in the sample solutions is attributed to the additional C (~ 4 g L<sup>-1</sup>) supplied from bio-organic components in plasma specimens. The method detection limits for Mn, As, Cd, W, Hg, Pb and U were 0.0155, 0.00424, 0.00237, 0.00438, 0.00676, 0.00329 and 0.00207 μg L<sup>-1</sup>, respectively. For additional information check: Ryszard Gajek and Key-Young Choe, *J. Anal. At. Spectrom.*, 2015, Accepted Manuscript, DOI: 10.1039/C5JA00011D