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FRONTAL CHROMATOGRAPHY-ICP-MS: A NOVEL METHOD FOR FAST INORGANIC AS(III) AND AS(V) SPECIATION

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Analytical speciation methods for the trace determination of elements in different chemical forms have become increasingly important in the last decades. It is in fact well-known that the total concentration of elements cannot provide complete information about their impact on environmental and biological systems.

Routine speciation analysis are commonly based on the coupling of chromatographic separation techniques (e.g. HPLC) with a sensitive elemental detection system (such as ICP-OES or ICP-MS).

Since a large number of samples are usually analyzed with these routine methods (e.g. environmental samples, kinetic studies), the development of novel analytical protocols is favourable if an increase of the throughput together with a simplification of the required apparatus is delivered.

Since the partition coefficients of the species to be separated are usually markedly different, it is possible to simplify the instrumental apparatus by introducing a short column with a low number of theoretical plates instead of an HPLC system, with a consequent reduction of the analysis time. One advantage of this strategy relies on the low backpressure exerted by such short columns, which allows the feeding of the solution by a simple peristaltic pump (already present in all ICP-MS and ICP-OES instrumentation). Moreover, the exploitation of a frontal chromatography approach (i.e. a procedure in which the sample is fed continuously into the chromatographic bed) should avoid the presence of an injection valve, providing a further simplification of the overall system.

In spite of these considerations, the frontal chromatography still finds very little application for analytical purposes.

In light of this lack in the literature, we decided to make an investigation on the feasibility of a novel approach based on a frontal chromatographic system coupled with an ICP-MS to selectively analyze inorganic As(III) and As(V). Very preliminary data on this issue were already presented during the XXVII Congress of the Analytical Chemistry Division, while in this communication we would like to show the results concerning the fully developed method.

Briefly, complete frontal chromatograms can be recorded in around 160 seconds (Figure 1a) thanks to the introduction of a short column (60mm-long cartridge loaded with a strong anionic stationary phase) placed between the autosampler and the nebulizer. As(III) and As(V) are sufficiently well separated using this frontal chromatographic system, despite the low number of theoretical plates provided by the column.

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Multivariate and univariate methods were explored to accurately quantify As(III) and As(V). In particular, very good quantifications (relative errors in prediction under 3%) up to 135 ppb were obtained using PLS regression (Figure 1b-c). Additionally, LOD of 0.17 ppb for As(III) and 0.22 ppb for As(V) were estimated.

The actual time of analysis can be further reduced because accurate quantifications can be done using only the first 120 seconds of the frontal chromatograms. The simplification of the instrumental setup allows also to avoid time-consuming operations related to the employment of an injection loop (required for any HPLC-based method). Therefore, the resulting time of analysis is significantly lower than the ones reported in the literature for the fastest HPLC-ICP-MS inorganic As speciation methods [1].
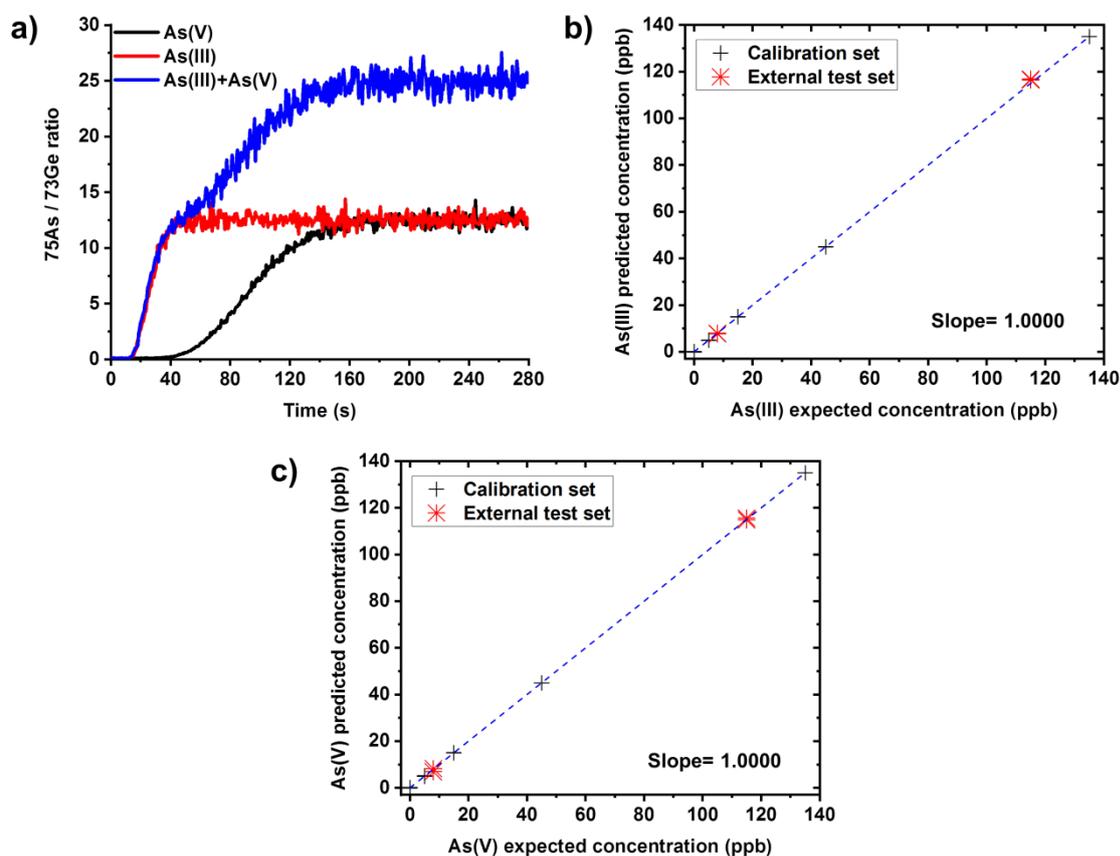

Figure 1. (a) Frontal chromatograms of a 135 ppb As(V) solution (black line), 135 ppb As(III) solution (red line) and a mixture solution containing 135 ppb of both As(III) and As(V). In all the measurements Ge was used as internal standard. (b-c) Expected vs. Predicted concentration plot for As(III) (Figure b) and As(V) (Figure c) obtained by PLS regression.

References

[1] Marcinkowska M., Komorowicz I., Barałkiewicz D., Talanta, 2015, 144, 233-240.