Correction of interferences caused by oxide and hydroxide analyte species in ICP-MS: development and limits of a new method applied to transition metals

S. Aries
M. Valladon
M. Polvé

Géochimie - UMR - CNRS 5563 - Univ. P. Sabatier - 38, rue des 36 ponts - 31000 Toulouse, France

When using ICP-MS, the presence of oxide and hydroxide analyte species in the argon plasma can introduce strong errors in the calculation of concentrations, specially for *REE* and transition metals.

The formation of such oxide and hydroxide species, due to the presence of water in the solution, takes place in the boundary layer around the edge of the sampling cones (Vanhaecke *et al.*, 1992). Some authors (Vaughan *et al.*, 1986,...) have shown that those oxide and hydroxide formations depend on machine parameters like sampling depth, plasma power, nebuliser and carrier gas flows...Those parameters have to be optimised to minimise oxide production rate.

The aim of our study is to determine the concentration of transition metals in environmental and geological samples. When analysing such samples, matrix components like Ca, Ti, Si,... form oxides and hydroxides and artificially enhance signal and then the concentration of some transition metals. For example, the $^{60}Ni^+$ signal is enhanced by $^{44}Ca^{16}O^+$ and the $^{62}Ni^+$ signal is enhanced by $^{46}Ti^{16}O^+$. The choice of only one isotope for analysing these metals is not reliable.

The relative importance of the oxide production rate is correlated with the oxide bond strength (Dulski, 1994, Vanhaecke *et al.*, 1992,...). Shibata *et al.* (1993) demonstrate, from theoretical calculations involving thermodynamical and spectroscopic data, that a linear correlation exists between log (MO^+/M^+) and the dissociation energy of the MO bond. Moreover, they show that this relation is controlled by oxygen partial pressure in the plasma and plasma temperature.

We have determined the MO^+/M^+ ratios for several elements in monoelemental solutions with an ICP-MS (Elan 6000, Perkin Elmer). Then, we have plot the log (MO^+/M^+) versus M-O bond strength (data taken from *Handbook of Chemistry and Physics*, 1980). The figure shows a good linear correlation (r = 0.92). The MOH^+/M^+ ratios have also been determined, and have shown similar variations than MO^+/M^+, indicating the same behaviour.

This linear correlation implies that the ratio K = $(MO^+/M^+)/(M'O^+/M'^+)$ is a constant for given conditions of plasma. This is also true for the K' = $(MOH^+/M^+)/(M'OH^+/M'^+)$ ratio. This means that, in the sample, the determination of an oxide and an hydroxide production rate permits the determination of all the others. Measuring these production rate, directly in the samples, allows to take into account possible variations of matrix effects from a sample to another.

M' can be any element but we chose Ce or Ba because their oxide production rate can be measured directly in each sample (Valladon *et al.*, 1995). We have built up a data set of K and K' values for all elements of interest.

Assuming that the plasma conditions remain constant, for each sample we can calculate the contribution of MO^+ and MOH^+, by using our K and K' data set and by determining:

- M^+ in the sample. M is the interfering element (Ca, Si, Ti,...).
- CeO/Ce and CeOH/Ce or BaO/Ba and BaOH/Ba in the sample.

For each element M, we can write the following type of equation:

$$Im = M - M_{-16}O - M_{-17}OH$$

where Im is the intensity measured at the mass M, M is the contribution to Im of the isotope of mass M of the element, $M_{-16}O$ is the contribution of the isotope of mass M-16 of an interfering element, $M_{-17}OH$ is the contribution of the hydroxide of the isotope of mass M-17 of an interfering element.

So, knowing the values MO^+ and MOH^+, we can calculate the contribution of the M^+ signal to 'Im'
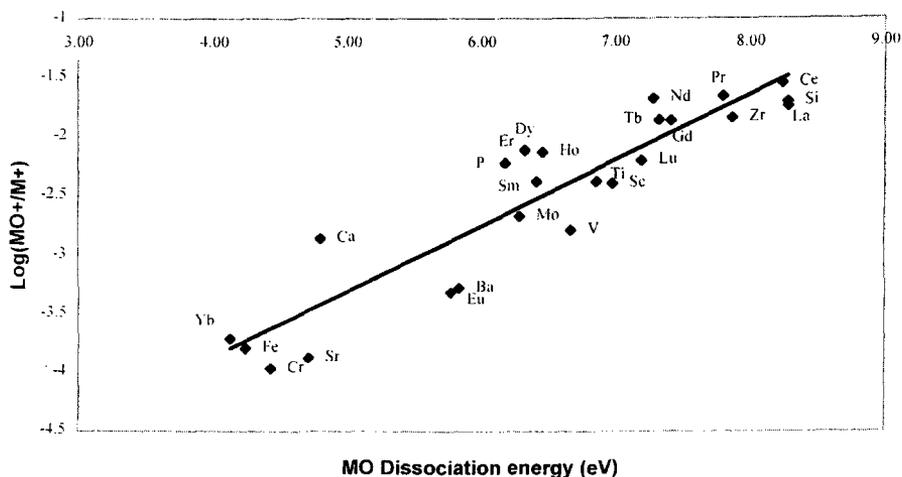
FIG. 1. Log (MO^+/M^+) *vs* MO dissociation energy.

and then eliminate interferences caused by oxides and hydroxides.

This method is currently applied to the determination of *REE* concentrations (Valladon *et al.*, 1995) in our laboratory and gives good results. We will show the development and the limits of the method when applied to the determination of transition metals by analysing certified standards.

References

Dulski P. (1994) *Fresenius Journal of analytical Chemistry*, **350**, 194–203.

Handbook of chemistry and physics (1980–1), 61st edition CRC Press.

Shibata, N., Fudagawa, N. and Kubota, M. (1993) *Spectrochim. Acta*, **48B, 9** 1127–37.

Valladon, M., Dupré, B. and Polvé, M. (1995) *EUG 8 Strasbourg*, Terra abstracts supplement n°1 to *Terra Nova*, **7**, 347.

Vanhaecke *et al.* (1992) *Mikrochimica Acta*, **108** 41–51.

Vaughan, M.A. and Horlick, G. (1986) *Appl. Spectrosc.*, **40,4** 434–45.