Analytical Methods

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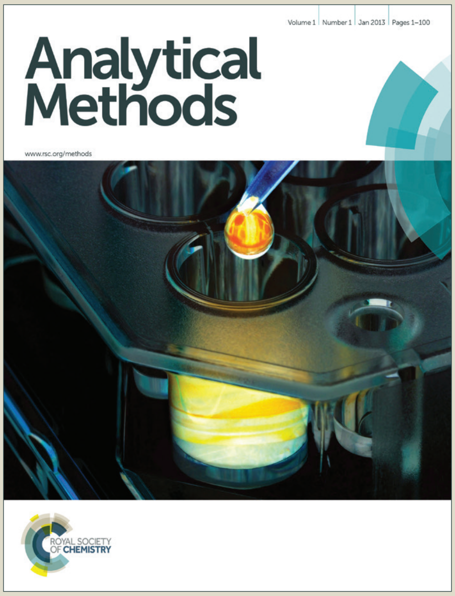
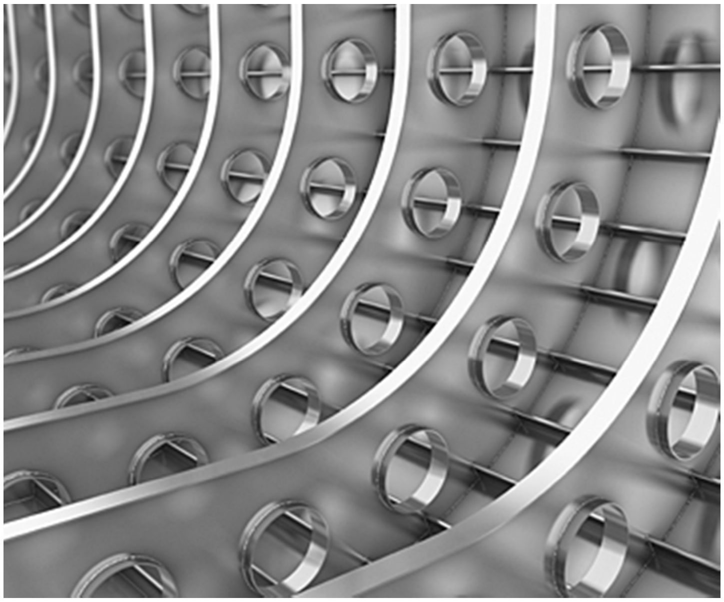


It is possible to obtain consistent niobium concentrations in a wide range of natural waters by ICP-SFMS without preconcentration



TECHNICAL NOTE

Direct determination of niobium at the low nanogram level in mineral waters and freshwaters

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The increasing use of elements such as Nb and Ta in green and information technologies makes it necessary to develop appropriate analytical methods for studying their environmental and ecotoxicological behaviour. This paper describes the first time Nb has been directly identified in mineral and freshwaters, using inductively coupled plasma sector field mass spectrometry (ICP-SFMS). The scant values of Nb concentrations in freshwaters published include many values which are very close, or directly below, the detection limit of the technique used; when low values are reported, the techniques used are often solid phase extraction preconcentration ones, with the associated problems of low blanks and potential incomplete resin desorption. We analysed 20 water samples of contrasting characteristics along with certificate reference material SLRS-5. Values detected ranged from 0.3 to 12 ng L^{-1}. No sample was below the detection limit. Our results show that the determination of Nb by ICP-SFMS is possible, although it is not a routine analysis (i.e., it requires excellent blanks and machine response stability). These results are consistent with existing information. Currently, Nb ecotoxicological characteristics and behaviour in environmental compartments are essentially unknown; the possibility of directly determining Nb at these concentrations opens up new avenues for studying this element at meaningful environmental levels.

Introduction

Little (if any) information is available on the transformation and transport of Nb in different environmental compartments and even information on total content in the various environmental media is scarce and often contradictory (see Sup Info file). This situation is partly due to limited interest in the element historically but also to the lack of adequate analytical techniques. However, a number of elements that were formerly considered scientific curiosities, as is the case of Nb, have now become essential for new applications.[1] Some of these elements have received increased attention in recent years because of their scarcity and have been qualified as critical.[2,3]

About 89% of global Nb production goes into production of ferro-niobium, used in high strength low alloy steels. These are used in the manufacture of vehicle bodies, ship hulls, railway tracks and gas pipelines. The remaining 11% is used in the manufacture of Nb alloys, Nb chemicals and carbides and other Nb metal products. Applications range from ceramics and surface coatings to construction, engineering, electronics, medicine (e.g., MRI scanners), etc.[4] Even if, at first sight, such applications do not look prone to fostering diffuse pollution, dissipation losses of around 50% have been estimated for Nb between the life-cycle stages of manufacturing and end-of-life.[5] Thus, significant dispersion of Nb in the environment is to be expected in the near future.

Published concentrations for Nb in surface waters point to very low levels (see Sup Info file). Compared to other metallic elements, Nb is rather depleted in the continental crust; recent estimates of its abundance are around 12 ppm.[6] Although it is usually considered relatively immobile, some recent evidence suggests that it may be mobilised under certain conditions (waters rich in humic substances, Fe-rich groundwaters).[7] Niobium has no known role in biological systems and little is known about its toxicity. Curiously, considerable accumulation in some species of Ascidians has been reported.[8,9]

Traditional analytical methods for Nb (e.g., spectrophotometry using various reagents, ICP-AES, X-ray fluorescence spectrometry, and neutron activation analysis) were mostly developed for use with steels and geological materials where analyte levels are much higher than those expected in surface waters and matrices require harsh digestion methods. Recently, interest in studying the Nb/Ta ratio as a tool for the study of geochemical processes in the Earth's mantle[10] or the Zr/Nb ratio for constraining very early differentiation processes in the solar system[11] has led to an improvement of Nb determination by inductively coupled plasma mass spectrometry (ICP-MS). But, again, samples were very different from natural surface waters. On the other hand, analysis of a high number of mineral waters and freshwaters by ICP-MS in the frame of multi-element studies led to a very high number of below detection limit (BDL) values.[12-16] Subnanogram levels of Nb in seawater have been reported by a Japanese research group which applied ICP-MS with previous solid phase extraction.[17-19] Since preconcentration techniques are always time-consuming and have the associated problems of low blanks and potential incomplete resin desorption, we have moved to testing the direct analysis by inductively coupled plasma sector field mass spectrometry (ICP-SFMS). It is well established that this is an extraordinarily sensitive analytical technique due to the much lower background signals and higher ion transmission.

Experimental

Samples

Study sites and mineral waters were chosen to ensure a broad variety water types in order to test the method. Sampling was performed according to strict protocols to avoid sample contamination. The only ancillary parameters measured when sampling were temperature and conductivity (Hanna HI98311-HI98312). Conductivity gives a quick and simple indication of the type of water.

Samples were not filtered and they were acidified to pH <2. Therefore, the Nb determined includes the dissolved fraction plus the part of the particulate fraction that can be easily dissolved under acidic conditions.

Reagents

Calibration standards were prepared through successive dilutions in cleaned Teflon bottles of 0.1 g L^{-1} ICP-MS stock solutions (AccuStandard). Suprapur® grade nitric acid (65% Merck) was used for the acidification and for the preparation of standards (2+1000). Ultrapure water was produced using the Milli-Q® Ultrapure Water System (Millipore, Bedford, MA, USA). Rh was used as the internal standard (IS) for samples and standards to correct signal drift; 100 µL of 100 µg L^{-1} Rh stock solution were added to 10 mL of standards and samples.

Instrument and operating conditions

The ICP-SFMS instrument used is a FinniganTM Element2 High Performance High Resolution ICP-MS, which consists of a double focusing reverse geometry mass spectrometer. The mass resolution was set to 500 in order to take advantage of the high signal transmission used in the low-resolution mode, thereby increasing the analytical sensitivity of Nb. The Element2 instrument was used with a standard glass spray chamber and Meinhard concentric nebulizer, under the operating conditions given in Table 1. Particular care was taken to ensure excellent conditions of machine response stability.

Results

Figures of merit

The sensitivity was higher than 1.2×10^{6} cps ppb^{-1} of ^{115}In in the low resolution mode (R=500). Repeatability values for the replicate measurements of Nb expressed as percent RSD was 3.8 % of 20 replicates, measured under the described experimental conditions at a concentration of 1 ng L^{-1}. The accuracy of the method was tested using a home-made standard solution containing 5.0 ng L^{-1} as a reference; it was 3.5%. The detection limit obtained for Nb determination in low resolution mode was around 0.02 ng L^{-1}. To achieve a quantification limit of about 0.1 ng L^{-1} for Nb determination in freshwater samples using the ICP-SFMS technique, care must be taken to optimize the ICP Nb response signal and to minimize noise with a view to obtaining an ICP blank response which is as low as possible.

Water Nb concentrations

Results obtained for the different water samples analysed are given in Table 2. Niobium concentrations range from 0.3 to 12 ng L^{-1}, which means that many values are well below the detection limit of previously published studies (see Sup Info). This implies that our values are consistent with the published data, where BDL values are prevalent, with percentages ranging from 20%[12] or 25%[13] for a detection limit of 2 ng L^{-1} up to 71%[14] or 89%[15] for a detection limit of 10 ng L^{-1}. It is worth mentioning that some of these studies gave median concentration values very close to the detection limit of the techniques applied (e.g., 4 ng L^{-1} for European stream waters (DL: 2 ng L^{-1}; 807 samples)[13] or 15 ng L^{-1} for streams in the Barents region (DL: 10 ng L^{-1}; 847 samples)[16]) and that these median values show a suspicious dependence on the detection limit of the technique applied. This is not an unknown behaviour but it does illustrate, once more, the need for high-performance analytical methods.

Particular mention needs to be made of the high value measured in Nürburg mineral water (417 ng L^{-1}). Similar high values had been reported for this water by Reimann and Birke[16] (201 ng L^{-1} in sparkling water in PET bottles and 537 ng L^{-1} for plain water contained in green glass bottles). These unusually high values seem to be due to these waters being of geothermal origin and pumped from high depths. Although orders of magnitude lower, our higher Nb concentration value for surface water is for a system in the same volcanic area, Maria Laach Lake, known for discharges of gases –mainly CO_2– of mantle origin within the water column.[20]

Unfortunately, the lack of standard reference materials with a certified value for Nb in surface waters means that it is currently not possible to confirm the accuracy of the results obtained. This a well-known, and insoluble, problem when developing analytical methods for analytes for which a standard reference material does not exist. Nevertheless, we applied the method to a standard reference material (SLRS-5 from the National Research Council Canada). The value obtained (2.8 ng L^{-1}) could be useful information for other laboratories measuring Nb concentrations in freshwaters.

Conclusion

Our results prove that it is possible to quantify Nb concentrations in freshwaters and mineral waters by ICP-SFMS without preconcentration. This possibility is extremely interesting because it will allow for rapid processing of a high number of samples while avoiding the problems associated with the use of preconcentration procedures. It also opens the door to laboratory studies where preconcentration might pose a problem such as, for instance, the determination of thermodynamic parameters or the study of Nb complexation by natural ligands (natural organic matter, mineral particles) at environmentally-relevant concentration levels.

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Table 1 HR-ICP-MS operating conditions

Incident Rf power	1.2 kW
Plasma gas flow rate	15 L min^{-1}
Nebulizer gas flow rate	0.8 L min^{-1}
Cool gas flow rate	1.2 L min^{-1}
Accelerating voltage	5 kV
Mass resolution (10% valley)	500

Table 2 Niobium concentration in freshwaters and mineral waters

System	Type of sample	Conductivity / µS cm^{-1}	Nb concentration / ng L^{-1}
Lausanne, Switzerland	tap water	260	0.69
Luxembourg	tap water	485	0.86
Madrid, Spain	tap water	117	0.57
Spa	mineral water	54	0.32
Volvic	mineral water	207	1.00
Rosport Blue	mineral water	1912	0.69
Contrex	mineral water	2211	0.37
Kristall	mineral water	1230	1.19
Nürburg	mineral water	2927	417
Fensch, France	river water, source	678	1.0
Fensch, France	river water, upstream steelworks	1670	1.1
Fensch, France	river water, downstream steelworks	1644	4.1
Small stream, Lorraine, France	river water, running on derelict industrial soil	5530	4.1
Chiers, Niederkorn, Luxembourg	river water, close steelworks	1075	7.3
Alzette, Schifflange, Luxembourg	river water, close steelworks	731	3.1
Lake Geneva (Vidy, Switzerland)	lake water	274	2.0
Gemundener Maar, Germany	lake water, volcanic area	54	1.5
Weinfelder Maar, Germany	lake water, volcanic area	25	0.62
Schalkenmehrener Maar, Germany	lake water, volcanic ares	421	3.5
Maria Laach Lake, Germany	lake water, volcanic ares	660	11.7
SLRS-5	river water CRM		2.8