

# Zirconium interferences on the detection of silver nanoparticles by single particle ICP-MS: implications on natural water analysis

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## Methodology article

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# Abstract

**Background:** The analysis of silver nanoparticle (NP-Ag) by the single particle technique with argon plasma-coupled mass spectrometry (SP-ICP-MS) is an increasingly used analytical approach. The sensitive technique, distinguishing particle size distribution, allows working at concentrations similar to those found in environmental samples. The two natural Ag isotopes 107 and 109, with abundances of 52 and 48% respectively, have similar sensitivity in ICP-MS detection. However, it is common to encounter isobaric interferences in mass spectrometry, and the element silver is not an exception, as much with the 107 isotope as 109. For both isotopes, zirconium oxides present isobaric interferences, either  $91\text{Zr}16\text{O}$ ,  $90\text{Zr}16\text{O}1\text{H}$  for the isotope 107 and the  $92\text{Zr}16\text{O}1\text{H}$  for the 109.

**Results:** For surface water analysis by ICP-MS in regular technique, these interferences do not generally impact the analysis of total Ag concentrations (mainly dissolved) as they can be then simply subtracted like background signal. On the other hand, detection of NP-Ag was impacted by the interfering colloidal Zr. The analysis of Zr by the SP-ICP-MS technique of surface waters showed the presence of colloidal Zr, a random signal that cannot be simply subtracted from NP-Ag signal. Our results show that, Zr colloids are effectively interfering with the NP-Ag assays by SP-ICP-MS technique where interferences translated into a false positive.

**Conclusion:** The analytical issue related isobaric interferences from the naturally occurring colloidal Zr was attenuated (up to 250% in this assay) by the use of the 109 isotope in the Ag detection, limiting false positive detections and improving the reliability of NP-Ag measurements in natural waters. Therefore, more specific detection of NP-Ag in surface waters that naturally contain Zr colloids can be accomplished.

## Background

The occurrence of silver (Ag) in urban effluents is associated with the increasing use of silver nanoparticles (NP-Ag) as an antiseptic agent frequently used in clothes and in food [1, 2]. When municipal effluents are discharged into receiving streams, they are contaminated by both "dissolved Ag" and NP-Ag forms. Such distinction among Ag forms must be taken into account in the assessment of exposure and toxicological effects to aquatic organisms [3]. Their environmental monitoring, both in effluents and aquatic ecosystems, requires a sensitive analytical approach that will allow the differentiation of NP-Ag from dissolved Ag. Argon plasma-coupled mass spectrometry (ICP-MS) is commonly used for the analysis of total Ag at low levels. These sensitive instruments are also used with the single particle technique (SP-ICP-MS) to distinguish forms between NP-Ag from the dissolved phase. This specific technique consists in the collection of a series of measurements passing in the order of the millisecond for at least one minute in the detector system [4, 5]. The dissolved phase distributed evenly in the solution generates a constant signal, while the passage of a NP-Ag into the plasma is characterized by an intense signal for a very short period of time (0.0005 ms). The intensity of this signal is proportional to the particle size. A very short reading time of the order of the millisecond (ms) allows the

SP-ICP-MS to record this signal (Fig. 1). A subsequent mathematical treatment of all the collected signals allows the separation and quantification of the two Ag forms [5, 6].

The analysis of Ag by ICP-MS presents isobaric interferences, both with the Ag isotopes 107 and 109, due to the presence of natural zirconium (Zr) in the sample. The isotope 107 is frequently used for the detection of NP Ag in various environmental samples [7, 8]. For the isotope 107, the interfering elements are  $^{91}\text{Zr}^{16}\text{O}$  and  $^{90}\text{Zr}^{16}\text{O}^1\text{H}$ , while the elements  $^{92}\text{Zr}^{16}\text{O}^1\text{H}$  for the isotope 109 [9, 10]. In natural waters, the Zr concentration was not found as abundant and generally  $< 1.0 \mu\text{g/L}$  [11] so that the interferences with the total Ag analysis are weak. Zirconium is not considered as a highly soluble element [12] and is rather found in the form of a suspended particle or colloid in water. In ICP-MS analysis in regular mode, isobaric interferences can thus be subtracted from the total concentration measured if the total Zr concentration and its correction factor are known. In the natural water samples analyzed in our laboratories, the total Zr concentrations were generally  $< 1.0 \mu\text{g/L}$ , and the interferences with the total Ag analysis are typically low and even below the detection limit. The analysis of particulate or colloidal Zr in natural waters by the SP-ICP-MS technique however has to generate signals of the same nature as Ag nanoparticles.

In single particle (SP) analysis mode, the interfering in the dissolved form would be present throughout all the reading of signals and would be included in the background, which would be subtracted prior the size calculations of the particles different from background. For the assessment of the NP, the background signal is subtracted from the intensity of the peak generated by NP and is not involved in the calculation of the size. However, in SP-ICP-MS mode with the interfering in particulate form, the induced Zr interference would be similar to the signal of a Ag particle and could not simply subtracted since randomly distributed. The detection of NP  $^{107}\text{Ag}$  in significant concentrations in natural waters compared to wastewater effluents may raise questions about their occurrence and interferences from natural suspended particles [7]. In this study, we thus propose to determine the interference of particulate and colloidal Zr on the detection of NP-Ag in natural waters by SP-ICP-MS using both natural 107 and 109 Ag isotopes.

## Results And Discussion

### *Evaluation of isobaric interferences of Zr on silver isotopes 107 and 109*

The intensities of the Ag109, Ag107, and Zr90 isotopes were measured in the ionic Zr solution (10  $\mu\text{g/L}$ ). The intensity (cps) ratio of Ag107/Zr90 and Ag109/Zr90, respectively 0.393% and 0.023% indicated the rate of Zr interference on silver measurements. Calculated ratios should not be considered constant, as they are strongly associated with the instrument optimization, specifically regarding the cerium oxide formation. In this study, ICP-MS parameters were optimized according to the manufacturer's specifications: CeO/Ce ratio below 2%. The detection of isotope Ag107 was thus much more interfered by Zr than the 109 isotope as indicated by Guo and al. [10] for the determination of total Ag concentrations by regular mode. Given that the two natural isotopes of silver are in similar proportions, 52% for the 107 and 48% for 109, we thus benefited from using the isotopes choice as shown in figure 1

for the analysis of NP Ag standards. The 107 isotope is rather recommended and frequently used for both routine analyses in regular and single particle ICP-MS modes [7, 8, 13, 14]. In SP mode for NP analysis, the selection of Ag isotope should however be investigated with respect to the Zr interferences.

### ***Analysis of a solution of NP-ZrO<sub>2</sub> by the technique of SP-ICPMS.***

Figure 2 shows the analysis of a solution of NP-ZrO<sub>2</sub> using the isotope 90 of the Zr and the two Ag isotopes, 107 and 109, by the technique SP-ICP-MS. A study by Deguelde et al. [4] showed the feasibility of the analysis of colloidal ZrO<sub>2</sub> by the SP-ICP-MS technique using its isotope 90. The figure 2a shows the distribution of NP ZrO<sub>2</sub> analyzed in suspension solution (4 ug/L) by SP-ICP-MS technique using the isotope 90. The figure 2b reveals the analysis of this NP-ZrO<sub>2</sub> solution using rather the isotope Ag 107 while figure 2c was for the Ag109. Figure 2b shows a series of “fooling” peaks appearing similarly to signals for Ag particles. In contrast, the peaks with the 109 isotope of silver were much less intense (Fig. 2c). If the solution was contaminated with NP-Ag, the SP-ICP-MS analysis would have been able to measure similar intensities with the two Ag isotopes that typically occur in similar proportions. The figure 1 (a,b) shows the analysis of NP-Ag solutions by SP-ICP-MS with the two natural silver isotopes. The pulse intensities are similar with the two isotopes. NPs-ZrO<sub>2</sub> interfered with the detection of Ag particles by inducing false positives, especially with the isotope 107 (Fig 2b).

### ***Natural water Analysis***

Zirconium is naturally present in surface waters and mainly associated with the particulate and colloidal phase rather than the dissolved phase [11, 12, 15]. As previously mentioned Zr interferes with the analysis of Ag and could overestimate the true Ag concentration (Fig. 3). In an aquatic system under natural erosion processes, significant concentrations of suspended particles are typical in surface waters and Zr concentrations were evaluated at <1 µg/L (Table 1). Considering that to have an interference, a false positive, on the detection of a nanoparticle it is necessary that the interference comes from the particulate phase. The analysis of particulate Zr in natural waters by the SP-ICP-MS technique would thus produce signals that can be confused with silver nanoparticles; so there is a likelihood of a false positive.

Total silver concentrations measured with the Ag isotopes 107 and 109 were similar, despite the presence of 700 ng Zr total/L in the sample (Table 1). The difference between the two Ag isotopes was below the detection limit (1 ng/L). For the quantification by ICP-MS in regular mode (i.e., for total Ag concentration),

it was therefore concluded that the contribution of Zr interferences is marginal on the determination of total silver concentration in these natural waters.

On the other hand for the NP quantification, Figure 3a shows different Zr intensity distribution for the natural water analysis with the SP-ICP-MS technique. Figures 3b and 3c show the measurements of silver particles in natural water evaluated with isotopes 107 and 109 of silver. For these last two figures, the results are presented as spherical particle sizes calculated from the intensities measured. Figure 3a shows that the natural water contains Zr particles with the presence of intense peaks corresponding to particulate Zr. Figures 3b and 3c distinguished the presence of silver particles by comparing 107 and 109 isotopes. Series of natural water samples were analyzed by the SP-ICP-MS technique and figure 4 shows results on the determination of NPs. For each assay, the number of silver particles larger than 30 nm (size threshold) was calculated for silver isotopes 107 and 109. The figure 3 highlights that there is much more detection with the 107 isotope when compared to 109. In an assay, 25 particles were detected using the isotope 107 while only 9 were detected with the isotope 109 (Fig. 4). If it would have been only silver particles, the number of detection should have been similar between the two isotopes utilized. Measurements with isotope 107 thus have false positives due to detection of  $^{91}\text{Zr}^{16}\text{O}$  and  $^{90}\text{Zr}^{16}\text{O}^1\text{H}$  originating from particulate Zr.

Thereby, because of higher detection specificity, the isotope  $^{109}\text{Ag}$  was selected for NP-Ag analysis in water samples. In regular ICP-MS detection mode analysis (i.e., for total Ag concentrations), the Zr isobaric interferences have minor impacts on measured concentrations and could be simply subtracted from the total concentration as long as the Zr concentration and its correction factor are known. On the other hand, in the case of analysis by SP-ICP-MS (i.e., for NP analysis), this signal correction procedure is not possible since the signal generated by a particle is random in time. With this technique, the results are expressed in a number of NP/ml rather than a mass of NP/ml. The interference generated by the particulate Zr would thus be read as a false positive. To minimize the presence of false positives a threshold of intensity was calculated to avoid these problems. With the analysis of the  $^{90}\text{Zr}$  by SP-ICP-MS, the maximum pulse intensity was measured for the particulate Zr signal ( $6 \times 10^6$ ), which was then converted to  $^{109}\text{Ag}$  intensity equivalent multiplying the intensity of it by the interference rate roughly corresponding to NP-Ag with size in the order of 27 nm. As a conservative approach, NP-Ag smaller than 30 nm were therefore not considered in the assessment. With the isotope 107, the signal generated by Zr particle would even correspond to a particle of 60 nm, justifying the setup of a safe detection threshold of 30 nm with the silver isotope 109.

# Conclusions

For accurate detection of NP Ag (i.e., avoiding false positives), it is necessary to take into account the abundance of particulate Zr and to consider the likelihood of a false positive. The analysis of surface water samples by SP-ICP-MS confirmed the presence of Zr particles. This particulate Zr phase would interfere with the analysis of Ag nanoparticles and may overestimate the number and concentration of Ag particles. In order to increase the reliability of the analysis of Ag nanoparticles, the particulate Zr interference was verified for both Ag isotopes. Our results showed that for a given Zr particle the interference on the  $^{107}\text{Ag}$  is greater than that on  $^{109}\text{Ag}$  isotope. For greater reliability of the analysis, the isotope  $^{109}\text{Ag}$  was thus selected for the analysis of NP Ag in natural water samples.

The analysis of Zr by the SP-ICP-MS technique provided the maximum size of false positives to be calculated from the intensity of Zr peaks. Based on intensities of Zr pulses measured in SP-ICP-MS mode and the calculated Zr oxide content, a silver nanoparticle detection confidence limit size was estimated. Using the  $^{109}\text{Ag}$  isotope, this confidence size threshold was set as a particle size of 30 nm for this type of natural water. All signals of particulate forms below this size have a probability for false positive and should not be considered in final results as confirmed nanoparticulate forms. We suggest that for silver particle analysis in natural water samples by SP-ICP-MS, silver isotope  $^{109}\text{Ag}$  be preferred. In addition, a solution of Zr should be analyzed to calculate the level of interference on isotope  $^{109}\text{Ag}$  while natural waters should be analyzed for the  $^{90}\text{Zr}$  by SP-ICP-MS mode to determine maximum of intensities from  $^{90}\text{Zr}$ . Though these Zr interferences do not have potential impacts on the determination of total Ag concentrations in natural waters, false positive detection using Sp-ICP-MS must be considered in the measurement of NP-Ag.

## Experimental

### General information

The NP-ZrO<sub>2</sub> was purchased from Sigma Aldrich (643122). The particle sizes are less than 100 nm and the concentration is 5 wt%. A solution of 4 ng Zr / L in Milli-Q water was prepared by a series of successive dilutions. This solution was analyzed for Zr, with  $^{90}\text{Zr}$  isotope, and for the both natural silver isotopes,  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$ , with SP-ICP-MS mode. Before analysis, samples were sonicated in ultrasound bath. The stock solutions of NP-Ag were purchased from TED PELLA (84050-80) and were in solution of sodium citrate (1 mM) as citrate allows for much longer storage of NP-Ag. The particle size was  $78 \pm 9$  nm. The initial total Ag concentration of the solution was 21 000  $\mu\text{g Ag total/L}$ . By serial dilutions, a 4.2 ng/L working solution was prepared. All prepared, sonicated NP-Ag solution was in sodium citrate (1 mM) solution and analyzed for NP-Ag content using  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  silver natural isotopes. The natural proportion of  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  silver isotope was respectively 51.8 and 48.2%.

The Ag and Zr 10000 mg/L ionic standard were purchased from SCP Science (Baie-d'Urfée Montréal Canada). By serial dilutions, solutions of 0.1, 0.5 and 1.0 µg/L were prepared in 1 % HNO<sub>3</sub> (Baseline grade, SeaStar Vancouver Canada).

### **Nanoparticle determination**

The nanoparticles were measured by ICP-MS using the single particle technique (SP-ICP-MS) with a Thermo Scientific™ instrument (ICAP™-RQ). The transport evaluation, used for the size calculation [6], was done with the NP-Quant software provided by Thermo Scientific™®. The data processing was carried out with the Excel software. The acquisition time per event (dw) was set to 2.5 ms, for a total time of 60 s. Before the nanoparticle analysis, the instrument was optimized with tune solution (1 µg/L: Ba, Bi, Ce, Co, In, Li, U in 2.5 % HNO<sub>3</sub> and 0.5 % HCl) to obtain the maximum sensitivity, the ratios Ba<sup>++</sup>/Ba<sup>+</sup> < 3% and the CeO/Ce < 2%.

### **Isobaric interferences evaluation**

The determination of zirconium-induced polyatomic ion levels on silver 107 and 109 isotope signals, we prepared and analyzed an ionic Zr solution (10 µg Zr/L). The intensity measurements, expressed in cps unit, of isotopes 90 of Zr and 107 and 109 of Ag were measured. The intensity ratio <sup>107</sup>Ag/<sup>90</sup>Zr and <sup>109</sup>Ag/<sup>90</sup>Zr correspond to the contribution of formed Zr oxide and hydroxide ions to silver 107 and 109 isotope signals, respectively.

### **Natural water analysis**

A series of analyses (n=10) were performed on surface water samples taken on May 18, 2018 in the St. Lawrence River in front of Quebec city. Samples were analyzed for suspended particulate matter (SPM : 27 mg/L) and dissolved organic carbon (DOC: 4.59 mg/L). The SP-ICP-MS technique (for NPs) was carried out for the determination of the Zr isotope 90 and the isotopes 107 and 109 of the silver. The three elements were alternately analyzed during a single sample aspiration for each replica. Simultaneous analyses of Zr and both Ag isotopes were performed at same time to minimize the sedimentation effect in test tube during the analysis. The total Ag and Zr concentrations (i.e., intensities of dissolved + NP) and the particle size were calculated with Excel software. For <sup>107</sup>Ag and <sup>109</sup>Ag intensities, we have calculated the equivalent spherical size with the equation described in previous studies [5, 6]. Total concentrations of each isotope element were evaluated by the intensity summation for each replica and comparison with ionic standard.

# Declarations

## Abbreviations

AgNPs: silver nanoparticles; ZrO<sub>2</sub> NP: zirconium oxide nanoparticles; SP-ICP-MS : single particle inductively coupled plasma–mass spectrometry

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## Authors' contributions

PT and CG designed the research. PT performed the research. PT and CG analyzed the data. PT and CG contributed the reagent/material/analysis tools. PT and CG wrote the paper. All authors read and approved the final manuscript.

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## Availability of data and materials

All data and material analyzed or generated during this investigation are included in this manuscript. The raw data can be requested by emailing : [Christian.gagnon@canada.ca](mailto:Christian.gagnon@canada.ca)

## Competing interests

The authors declare that they have no competing interests.

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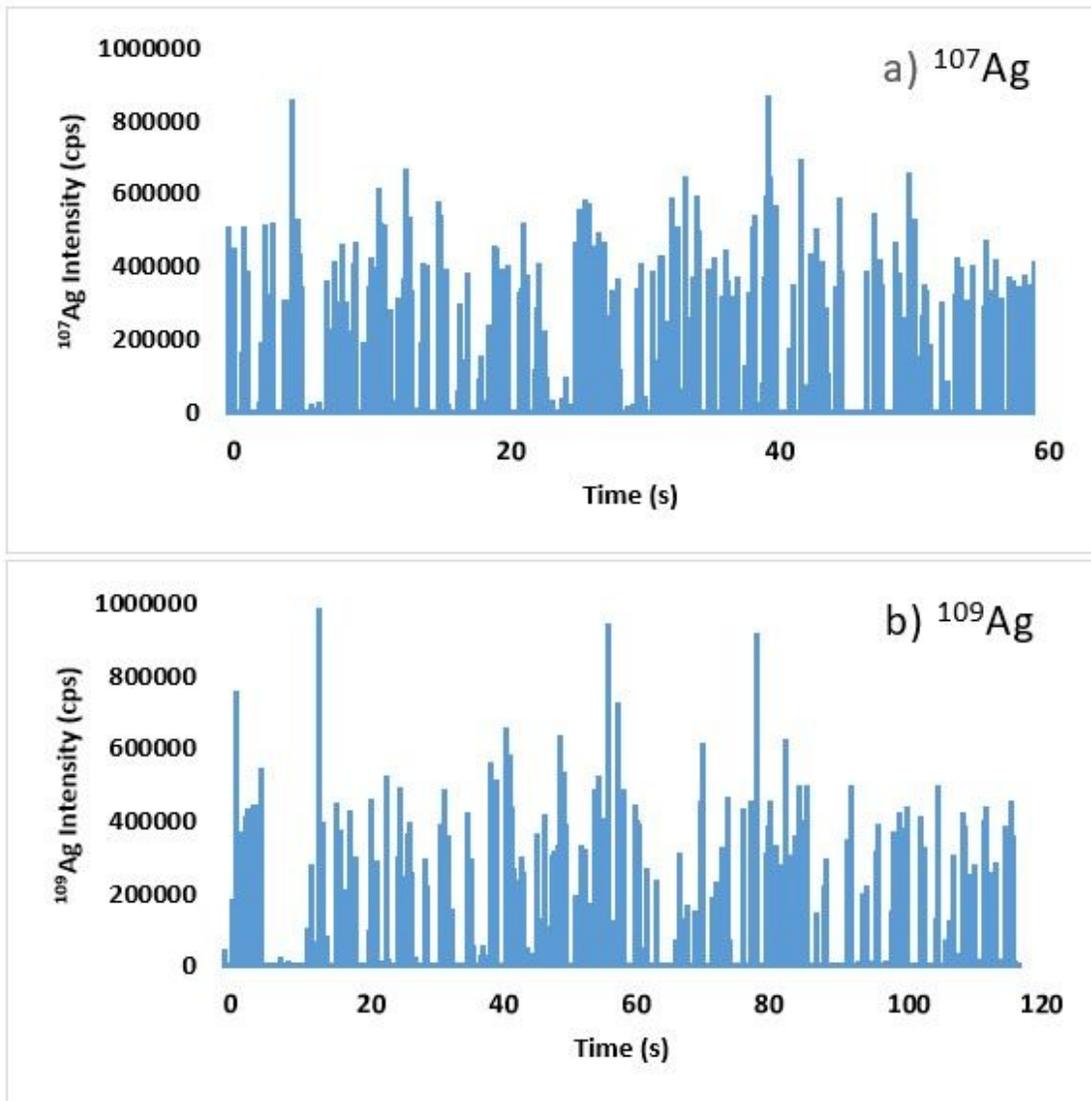
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## Table 1

Id	Equivalent Ag total (µg Ag/L)			Zr total (µg Zr/L)
	<sup>107</sup> Ag	<sup>109</sup> Ag	<sup>107</sup> Ag- <sup>109</sup> Ag	<sup>90</sup> Zr
1	4.9	4.7	0.1	687
2	4.8	4.7	0.1	760
3	4.7	4.4	0.3	812
4	5.1	4.7	0.4	722
5	6.1	4.7	1.3	683
6	5.6	5.3	0.3	795
7	10	9.1	0.9	732
8	5.2	4.5	0.7	637
9	4.5	4.3	0.2	654
10	4.9	4.3	0.6	642

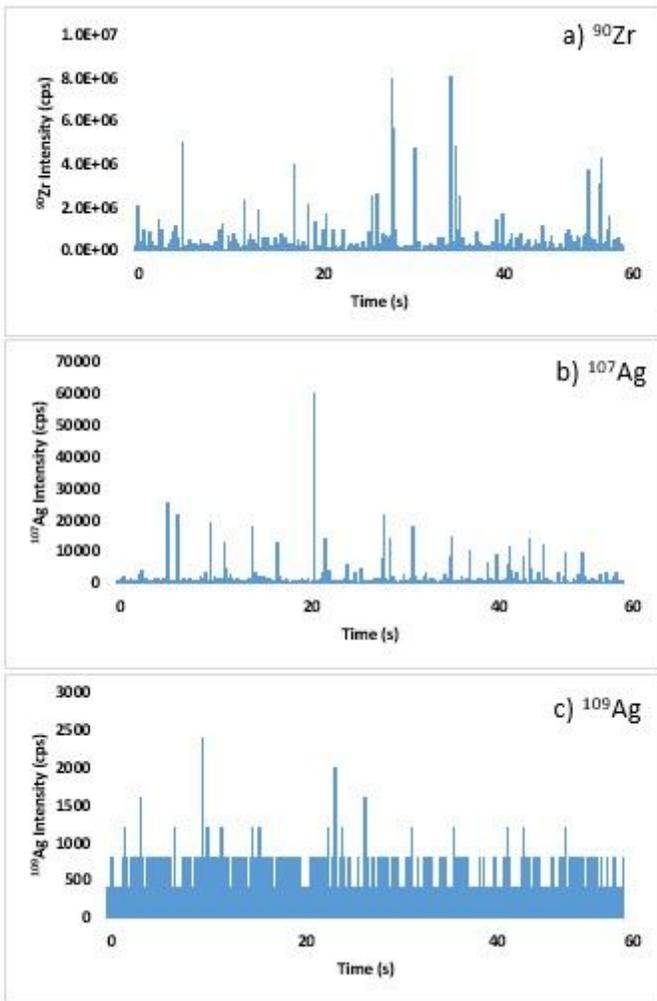
Table 1. Analysis of surface water (Total concentration determination in a series of assays)

## Figures



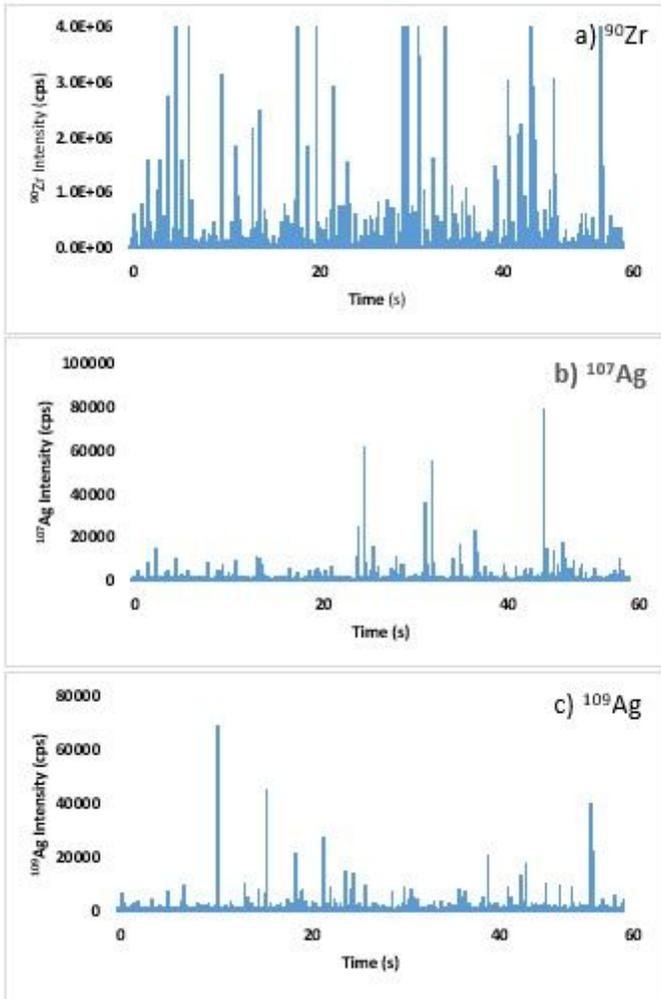
**Figure 1**

Silver nanoparticle analysis in SP-ICP-MS mode with the 107 (a) and 109 (b) silver natural isotope; diluted NP Ag standard solution.



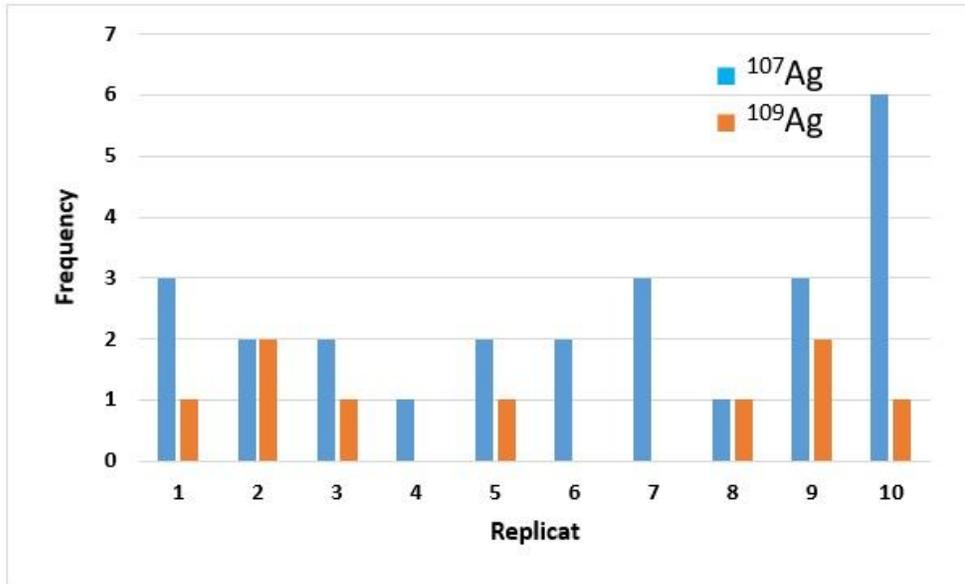
**Figure 2**

Zirconium oxide nanoparticle analysis in SP-ICP-MS mode with the  $^{90}\text{Zr}$  (a),  $^{107}\text{Ag}$  (b) and  $^{109}\text{Ag}$  (c) isotopes



**Figure 3**

Natural water analysis in SP-ICP-MS mode with the  $^{90}\text{Zr}$  (a),  $^{107}\text{Ag}$  (b) and  $^{109}\text{Ag}$  (c) isotopes.



**Figure 4**

NP-Ag > 30 nm analyses with the both silver natural isotopes,  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$ , in 10 natural water replicates.