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ARTICLE

Lead determination by HG - MIP OES with nitrogen plasma, after variables optimization study

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A hydride generation nitrogen microwave induced plasma optical emission spectrometry (HG – MIP OES) system was developed for lead determination. Plumbane chemical generation was performed using 0.045 mol L⁻¹ K₃Fe(CN)₆ as the additive in acidic medium and 2.0 % w/v NaBH₄ in 1% w/v NaOH as the reductant. The additivated sample and the reductant were pumped towards a cyclonic chamber where hydride generation and separation from the solution occurred. Operating conditions such as additive and reductant concentration, sample, reductant and nitrogen flow-rate, the cyclonic chamber stabilization time and the viewing position in the torch were optimized. A meticulous study of the variation of the nitrogen plasma response as a function of the hydrochloric acid concentration was carried out. The analytical performance of the method was studied and its applicability evaluated in a Trace Element in Water Certified Reference Material and a soil Reference Material. The method performance in terms of limits of detection and quantification (0.54 µg L⁻¹ and 1.8 µg L⁻¹ Pb respectively) were found comparable to others atomic spectrometry techniques. This is to our knowledge the first research of the analytical performance of lead determination by PbH₄ generation and determination by MIP OES.

Introduction

Lead occurs in the Earth's crust associated with other elements; the industrial processes release it to air, water and land. Adverse health effects are related to continuous low concentrations exposure. Even if several anthropogenic sources have been eliminated, its persistence in the environment makes exposure monitoring relevant due to its toxicological concern [1]. Hence, when selecting the analytical method for its determination, low detection limit techniques are required. Analytical atomic spectrometric techniques (i.e., atomic absorption (AAS), atomic emission (AES) and atomic fluorescence spectrometry (AFS)), coupled with chemical vapour generation (CVG) are suitable alternatives to fulfil this purpose [2].

CVG is a widespread sample introduction technique utilized in analytical chemistry. Hydride generation (HG) was the firstly reported for hydride forming elements such as As, Bi, Ge, Hg, Pb, Sb, Se, Sn and Te but was later extended to noble metals as

Au, Ag, Pd, Pt, Rd, Rh, and Os and other transition metals as Co, Cu, Cr, Fe, Ir, Mn, Ni, Rh, Ti, Zn [3-5].

Sodium tetrahydroborate (THB) has been the most common derivatization reagent used for HG. The HG mechanism depends on the reaction medium acidic concentration as it determines the prevailing reagent and analyte species in solution, and thus their mutual reactivity as well as the formed hydride stability [3,6,7].

However, in the case of lead, the direct reaction efficiency between Pb(II) and THB yielding lead tetrahydride (plumbane, PbH₄) is tiny. Its generation needs an additive with ligand/donor and/or redox properties which interact with the analyte and/or the THB producing an analytical useful reactivity modification [6,8]. D'Ulivo et al. largely studied its role in the PbH₄ generation, where hexacyanoferrate(III) is suitable for that purpose [6,8-10]. They postulated that hexacyanoferrate (III) formed a hydridoboron intermediate that reacts with Pb(II) enhancing its formation [8,9].

The volatile species once generated are driven towards the atomization device for its determination. Several detection systems have been coupled to the CVG: quartz tube atomic absorption spectrometry (QT AAS), probably the most used; electrothermal atomic absorption spectrometry (ETAAS);

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inductively coupled plasma optical emission spectrometry (ICP OES); microwave induced plasma optical emission spectrometry (MIP OES); and inductively coupled plasma mass spectrometry (ICP MS) [6,11-14].

MIP OES with nitrogen plasma is an interesting alternative technique to ICP OES able to be hyphenated with HG [15]. In 1987, Barnet [16] reported the first evidence of lead tetrahydride detection by MIP OES with helium plasma after HG with sodium persulphate. However, since the commercially available high-power MIP OES with nitrogen plasma in 2012 only a few studies have determined Pb by MIP OES; nevertheless, some used conventional chambers and others none clarified if it was done with or without hydride generation [17 – 23].

The microwave plasma (MIP) is created by nitrogen excitation through the combination of an axial magnetic field and a transverse electric one allowing a good interaction of the plasma and the sample, as well as higher plasma temperature. It reaches temperatures around 5000 K depending on the nitrogen flow-rate selected in the chamber and the plasma viewed position [21, 22].

For MIP OES analysis the hydride is generated in a multimode spray chamber (MSIS) which acts both as the generating compartment and gas-liquid separator. It consists of a glass cyclonic chamber fitted with two vertically opposed conical tubes where sample and reductant flows converge and mix in a thin film. A nitrogen flow strips the volatile species generated towards the torch. There are minimum transport losses as the cyclonic chamber is connected directly to the atomization device [14, 26 - 28].

To the best of our knowledge the first evaluation of MIP OES with nitrogen plasma for lead determination using hydride generation as the sample introduction technique is performed in this work. The chemical variables affecting the hydride generation and the instrumental parameters for its determination are presented as well as the analytical figures of merit for this methodology.

Experimental

Instrumentation

A microwave-induced plasma optical emission spectrometer MIP OES Agilent model 4210 (Agilent Technologies, Santa Clara, USA) equipped with a multimode spray chamber (MSIS, Agilent), and a standard torch was used for determination. An online nitrogen generator model 4107 (Agilent Technologies, Santa Clara, USA), which takes in air from the environment through an air compressor model KK70 TA-200 K (DürrTechnik, Bietigheim-Bissingen, Germany) was used.

A microwave-assisted digestion (Mars 6 CEM, North Carolina, USA) equipped with 12 Easy Prep Plus was used to prepare the soil reference material for lead determination.

Materials

A Millipore water purification system (resistivity 18.2 Mohm cm) was used to obtain deionized water. Lead working solutions were prepared daily by dilution of the corresponding 1000 mg L⁻¹ (Atomic absorption standard solution, Merck, Germany). The following reagents used were of analytical grade: potassium hexacyanoferrate(III), 63 % w/w nitric acid and 37 % w/w hydrochloric acid. Sodium tetrahydroborate solutions were prepared from sodium tetrahydroborate (hydride generation grade, Fluka) in 1% w/v NaOH.

Certified reference material, MRC.INO.101 Trace Elements in Water, was obtained from Laboratorio Tecnológico del Uruguay (LATU), Montevideo, Uruguay (2 % v/v HNO₃ medium, certified value: 34.48 µg L⁻¹ Pb).

Soil Reference Material: RM-Agro E2002a (Embrapa Pecuária Sudeste, São Carlos SP, Brazil). Reference value: Pb (mg kg⁻¹) 172.41 ± 4.02 (RSD% 2.33)

Sample preparation. Soil reference material was subjected to a microwave assisted acid digestion. Thereby, 0.35 g was treated with 10 mL of dilute HNO₃ (4.5 mol L⁻¹) using the following digestion program: heat to 200 °C hold at 200 °C for 15 min, and cool to room temperature (power 400–1800 W). The digestion of several complex matrices using a unique dilute acid (HNO₃) has been previously reported by our research group [29, 30]. Subsequently, the final volume was brought to 50 g with ultrapure water to decrease the original acidity. Reagent blanks were also run.

No sample preparation step was required for Trace Element in Water CRM and it was measured directly.

Analytical HG procedure

Lead solutions already containing the additive (0.045 mol L⁻¹ K₃Fe(CN)₆ and acid (HCl or HNO₃ as appropriate) and 2.0 % w/v THB were pumped towards the MSIS spray chamber at (0.90 mL min⁻¹). Triplicate measurements were performed during 5 s after the stabilization of the spray chamber with the PBH₄ generated for at least 20 s. The nitrogen flow-rate towards the plasma was about 750 mL min⁻¹ and viewing position 0. Lead determination was performed at 405.781 nm with automatic background correction. A general scheme of the described configuration of MSIS for PbH₄ generation and determination by MIP OES is shown in Figure 1.

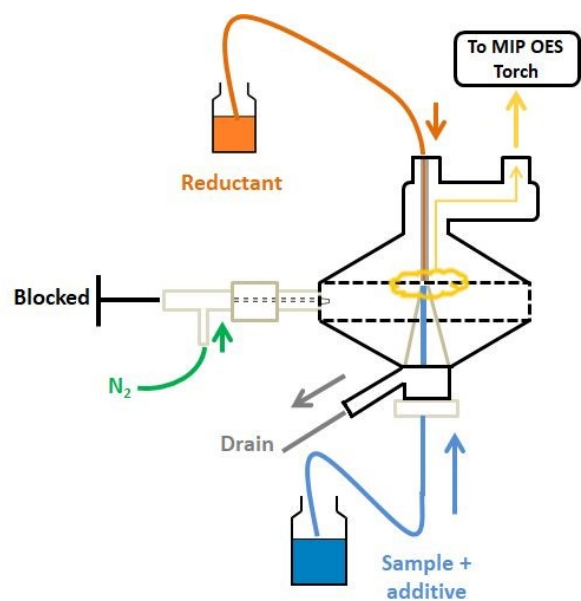


Figure 1: Scheme of the multimode spray chamber operating for plumbane generation.

Results and discussion

Plumbane generation: preliminary optimization

Several reagents are described in the literature as additives for PbH_4 generation [8, 10, 31 – 34]. In this work $\text{K}_3\text{Fe}(\text{CN})_6$ in acidic medium was chosen. The chemical variables studied were $\text{K}_3\text{Fe}(\text{CN})_6$, HCl and NaBH_4 concentrations. The reductant and sample flow-rates, and the instrumental parameters such as the stabilization time in the chamber, the nitrogen flow-rate and the viewing position in the torch were also evaluated.

The variables and the determining parameters were evaluated one at a time keeping the others constant. Conditions leading to the best signal intensity for PBH_4 were taken as the optimum criterion.

As a starting point, instrumental parameters and operating conditions were set as established by the manufacturer: N_2 flow-rate 0.75 mL min^{-1} , stabilization time 10 s, viewing position 0 and reagent flow-rate 0.45 mL min^{-1} . Chemical working conditions were chosen close to those found optimum in Kratzer work [10]. Three concentration levels were chosen for $\text{K}_3\text{Fe}(\text{CN})_6$ ($0.015 - 0.030 - 0.045 \text{ mol L}^{-1}$) and NaBH_4 ($0.4 - 1.0 - 2.0 \text{ \% w/v}$ in 1 % NaOH), and two concentration levels for HCl ($0.12 - 1.0 \text{ mol L}^{-1}$).

Table 1: Instrumental parameters and experimental optimized working conditions for Pb determination by HG – MIP OES with nitrogen plasma. DOI: 10.1039/D1JA00327E

Instrumental parameters		
Pump speed (rpm solutions flow-rate 0.90 mL min^{-1})	30	
Nitrogen flow (L min^{-1})	0.75	
Reading time (s)	5	
Viewing position	0	
Stabilization time (s)	20	
Wavelength (nm)	405.781	
Background correction	Automatic	
Experimental conditions		
$\text{K}_3\text{Fe}(\text{CN})_6$	HCl	NaBH_4 (*)
0.045 mol L^{-1}	0.12 mol L^{-1}	2.0 \% w/v

(*) Prepared in 1% w/v NaOH.

In the preliminary optimization process, THB concentration was kept fixed at 0.4 % w/v while each $\text{K}_3\text{Fe}(\text{CN})_6$ and HCl concentration combinations were run. The minor signal was found for 1.0 mol L^{-1} HCl at every ferricyanide level. Reagent (0.45 and 0.90 mL min^{-1}) and N_2 ($0.5 - 0.75 - 1.0 \text{ mL min}^{-1}$) flow-rates and the stabilization time of the cyclonic chamber (0, 10, 20 s) were sequentially assayed for each $\text{K}_3\text{Fe}(\text{CN})_6$ concentration level at 0.12 mol L^{-1} HCl. Next, for the aforementioned conditions leading to the highest signals, different viewing position in the torch ($-60 - -30 - 0 - 30 - 60$) were tried.

Finally, the reductant concentration ($0.4 - 1.0 - 2.0 \text{ \% w/v}$ in 1% w/v NaOH) was optimized. Table 1 summarizes the instrumental and working conditions which lead to the maximum signals.

Cheng et al. [34] reached similar results using HCl, indicating that at low acid concentrations Pb does not completely convert into hydride, while at high concentrations the hydride is diluted, observing in both cases lower signal intensity. From the preliminary optimization stage it follows that the variable of influence impacting most in the response was the HCl concentration. The study was focused then in the response up to that concentration seeking for further optimization.

Optimization of the acidic medium

To weigh up the effect of the HCl concentration in the determination of lead by HG – MIP OES with nitrogen plasma, the signals obtained at different acid concentrations were compared with the signal under the optimal working conditions found in the preliminary optimization study (0.12 mol L^{-1} HCl – 0.045 mol L^{-1} $\text{K}_3\text{Fe}(\text{CN})_6$). Solutions containing $50 \mu\text{g L}^{-1}$ Pb – 0.045 mol L^{-1} $\text{K}_3\text{Fe}(\text{CN})_6$ were prepared at increasing HCl concentrations within 0.05 and 1.15 mol L^{-1} (evaluated solutions) and run according to the analytical HG procedure described above together with a $50 \mu\text{g L}^{-1}$ Pb – 0.12 mol L^{-1} HCl

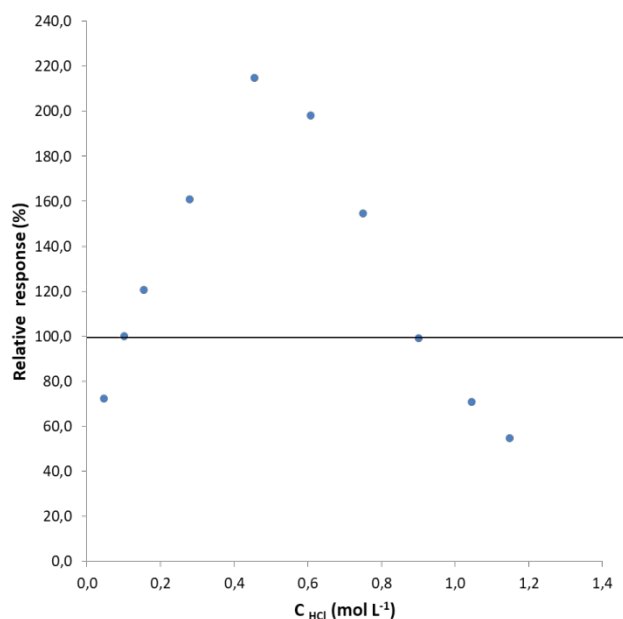


Figure 2: Variation of the relative response with increasing HCl concentration. The net signal of the 50 µg L⁻¹ Pb – 0.12 mol L⁻¹ HCl – 0.045 mol L⁻¹ K₃Fe(CN)₆ solution was taken as the reference. 2% w/v NaBH₄ in 1% w/v NaOH was used as the reductant.

– 0.045 mol L⁻¹ K₃Fe(CN)₆ solution. The signal of the latter was taken as the reference. The relative response was calculated as shown in Equation 1 and plotted against the hydrochloric acid concentration (Figure 2).

$$\text{Relative response (\%)} = \frac{\text{R evaluated solution}}{\text{R reference solution}} \times 100$$

Equation 1: R is the response (Intensity) measured under the instrumental conditions described in Table 1.

As could be observed, there is a signal enhancement within an acidic range of 0.12 and 0.90 mol L⁻¹, varying quite deeply in a narrow range of hydrochloric acid concentration, reaching an optimum close to 0.5 mol L⁻¹. At higher hydrochloric acid concentrations, probably the tetrahydride acidic decomposition overcomes the HG or the increased amount of hydrogen evolution due to the acidic decomposition of the NaBH₄ dilutes the hydride formed.

These results differ with regard to the ones met by other authors employing AAS. Elci et al. [35] and Ertas et al. [36] used 0.090 mol L⁻¹ K₃Fe(CN)₆, using a flow injection system and a continuous flow one for the HG, respectively; both found optimum acidic concentration at 0.036 mol L⁻¹ HCl.

Kratzer [10] used a continuous flow generation system for PbH₄ generation in 0.030 mol L⁻¹ K₃Fe(CN)₆ and found a signal enhancement up to 0.10 mol L⁻¹ HCl, a plateau up to 0.2 mol L⁻¹ HCl and a signal drop for higher acidic concentrations. Similar results were found by Bakirdere et al. [37] using the same K₃Fe(CN)₆ concentration in a batch system with an optimum signal at 0.16 mol L⁻¹ HNO₃ followed by a decay

which they attribute to the degradation of the ferricyanide. Nonetheless, Afonso et al. [36] used more concentrated ferricyanide, 0.090 mol L⁻¹ K₃Fe(CN)₆ and found the optimum acidic concentration quite close, at 0.091 mol L⁻¹ HCl for a continuous flow system by ICP OES determination.

Except for Ertas et al. who employed a quartz atom trap and made the determination by FAAS, and Afonso as previously mentioned, all the other authors accomplished the atomization in an externally heated quartz tube and the determination by AAS. It is well established that the H radical population in the quartz tube atomizer determines the atomization efficiency [6,11,39]. Atomization proceeds according to a radical mechanism for which high temperatures are not needed, just enough hydrogen to supply the radicals, however, a too high hydrogen flux can result in dilution of the volatile species and thus in a signal decay. High acidic medium results in high hydrogen evolution caused by the tetrahydroborate decomposition.

Among the literature, Ikeda et al. [40] was the only work who reported acidic conditions similar to this work. However, the generation system (continuous flow with two gas-liquid separators for plasma stability against hydrogen evolution), as well as the derivatizing agent (oxygen peroxide) are different, which makes the comparison difficult.

Petrov et al. [41] used a similar MSIS for the generation system as it was used in the present work. Oxygen peroxide was used instead of potassium ferricyanide and ICP - MS for determination, 0.1 mol L⁻¹ HNO₃ was found as optimum acidic medium.

Lead determination is usually performed after a wet digestion of the sample where nitric acid is frequently used either for this purpose or for liquid samples preservation. Envisaging the method applicability, the influence of HNO₃ concentration in the response was also evaluated. The response of 50 µg L⁻¹ Pb – 0.045 mol L⁻¹ K₃Fe(CN)₆ solutions in (0.12 – 0.30 – 0.75 – 0.90 – 1.20) mol L⁻¹ HNO₃ was compared towards the response of 50 µg L⁻¹ Pb – 0.045 mol L⁻¹ K₃Fe(CN)₆ solutions in (0.12 – 0.30 – 0.75 – 0.90 – 1.20) mol L⁻¹ HCl. For that purpose the relative response for each solution was calculated according to Equation 1. As previously mentioned, the reference solution was 50 µg L⁻¹ Pb – 0.12 mol L⁻¹ HCl – 0.045 mol L⁻¹ K₃Fe(CN)₆ both for hydrochloric and nitric acid solutions.

Results are presented in Table 2. The difference in the relative response found when the acidity of the medium came from HNO₃ was less than 10 % the one obtained for HCl in the acidic concentration range where there is no signal detriment. Hence, using HCl or HNO₃ would arise similar results.

Table 2: Comparison of the relative response of a 50 $\mu\text{g L}^{-1}$ Pb – 0.045 mol L^{-1} $\text{K}_3\text{Fe}(\text{CN})_6$ solution at different HCl or HNO_3 concentrations.

HCl / HNO_3 (mol L^{-1})	Relative response (%) HCl	Relative response (%) HNO_3
0.12	100.0	101.5
0.30	201.3	194.2
0.75	154.6	146.3
0.90	99.1	104.0
1.20	54.7	47.2

Among 0.12 and 0.90 mol L^{-1} HCl or HNO_3 have a positive impact on the HG which in terms of acids usually added to samples corresponds to (1.0 – 7.5)% v/v HCl or (0.8 – 6.0) % v/v HNO_3 . The signal variation is wide in a quite narrow range of acidic concentration; hence, the calibration standards must have the same acidity as the samples in order to prevent biased results. Whenever possible, the calibration standards and the samples should be matched in a concentration range where the signal is as high as possible.

In samples requiring high nitric acid concentration digestions (above 6.0 % v/v) a neutralization and acidic concentration adjustment should be performed before achieving lead determination by HG – MIP OES with nitrogen plasma.

Analytical performance

The method was characterized according to the Eurachem Guide recommendations [42]. The analytical parameters of the proposed method such as linear range, limits of detection (3s) and quantification (10s), precision (repeatability) and trueness were evaluated to determine its applicability.

According to the results obtained about the relevance of the acidic concentration in the sample, the characterization was carried out at the same CRM acidic concentration, taking advantage that it is a concentration for which the generation efficiency is high enough.

Linear range was evaluated up to 100 $\mu\text{g L}^{-1}$. The quantification was thus accomplished using a six-point external standards calibration curve in 0.28 mol L^{-1} HNO_3 . The LOD and LOQ were estimated from the standard deviation (s) of ten replicates of the reagent blank signal (0 $\mu\text{g L}^{-1}$ Pb – 0.28 mol L^{-1} HNO_3 – 0.045 mol L^{-1} $\text{K}_3\text{Fe}(\text{CN})_6$).

Precision under conditions of repeatability was calculated as the relative concentration standard deviation (RSD) of 6 replicates in Trace Element in Water CRM.

Table 3: Analytical performance of the HG – MIP OES with nitrogen plasma method for Pb determination.

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Linear range: 1.8 $\mu\text{g L}^{-1}$ - 100 $\mu\text{g L}^{-1}$	
Calibration function ($R^2 = 0.9995$): $I = 151.8 C + 132.6$	
Detection and quantification limits, n = 10	
LOD: 0.54 $\mu\text{g L}^{-1}$	LOQ: 1.8 $\mu\text{g L}^{-1}$
Precision (repeatability, n = 6) : 3.3 %	
Recovery (n = 6) \pm s: (89.5 \pm 2.9) %	

I: Intensity; C concentration ($\mu\text{g L}^{-1}$); LOD: limit of detection; LOQ: limit of quantification; s: standard deviation.

Trueness was assessed by means of Pb recovery after its determination by HG – MIP OES with nitrogen plasma in 6 replicates of the Trace Element in Water CRM (2 % v/v or 0.28 mol L^{-1} HNO_3 , 34.48 $\mu\text{g L}^{-1}$ Pb).

Results are presented in Table 3.

The methodology was also applied to analyse a soil reference material which was previously digested as already explained, diluted 50 times and acidified up to 0.28 mol L^{-1} HNO_3 . The recovery found was (90.7 \pm 4.6) % for two replicates.

A bibliographic research was carried out to compare the proposed methodology analytical performance with other frequently used. A comparison of Pb LODs found in the literature by other techniques is summarized in Table 4. The LOD found for HG - MIP OES with nitrogen plasma is comparable to those reached by HG and other atomic spectrometries, with the benefits of reducing costs per run considerably.

Conclusions

This is the first attempt that a novel Pb determination technique involving HG - MIP OES with nitrogen plasma is presented and its analytical performance determined. Experimental conditions were optimized and the relevance of the acidic concentration of the reaction medium was studied. The methodology has been successfully applied to the determination lead in water CRM and a soil RM. The LODs reached are suitable and in good compliance to those reported by other atomic spectrometries.

Table 4: Limit of detection (LOD) for lead determination by different techniques.

Technique	LOD ($\mu\text{g L}^{-1}$)	Reference
FAAS	10	[11]
MIP OES	7	[43]
ETAAS	1.7	[44]
HG – ICP OES	1.0	[40]
HG – AAS	0.56	[37]
HG – MIP OES	0.54	Present work
HG – ICP MS	0.20	[41]
ICP MS	0.18	[41]

FAAS: Flame Atomic Absorption Spectrometry, MIP OES: microwave induced plasma atomic emission spectrometry, ETAAS: electrothermal atomic absorption spectrometry, HG – ICP OES: hydride generation inductively coupled plasma atomic emission spectrometry, HG – AAS:Hydride generation atomic absorption spectrometry, HG – MIP OES: hydride generation microwave induced plasma atomic emission spectrometry, HG – ICP MS: hydride generation inductively coupled plasma mass spectrometry, ICP MS: inductively coupled plasma mass spectrometry.

The combination of HG and MIP OES with nitrogen plasma could be postulated as an advantageous and promising cost-effective alternative for Pb determination in waters and soils compared with high-cost instrumental techniques that require argon or acetylene. To the best of our knowledge this is the first research of the PbH_4 generation behaviour in acidic medium for determination by the MIP OES with nitrogen plasma system.

Author Contributions

Alicia Mollo: Conceptualization, data curation, formal analysis, investigation, methodology, project administration, supervision, validation, writing original draft.

Alexandra Sixto: Data curation, formal analysis, investigation, methodology, validation, writing review & editing.

Florencia Cora Jofré: Resources, visualization, writing review & editing.

Mariela Pistón: Resources, writing review & editing.

Marianela Savio: Conceptualization, resources, writing review & editing.

Conflicts of interest

There are no conflicts to declare.

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