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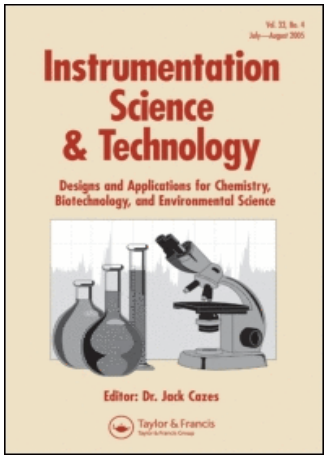

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On-Line Preconcentration and Analysis of Zinc in Water by Flow Injection-Knotted Reactor: Application to Geological and Environmental Exploration

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On-Line Preconcentration and Analysis of Zinc in Water by Flow Injection-Knotted Reactor: Application to Geological and Environmental Exploration

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Abstract: A preconcentration on-line system composed of flow injection (FI) and a knotted reactor (KR), associated with inductively coupled plasma atomic emission spectrometry (ICP-AES) has been used to determine Zn concentrations in river water. The zinc was retained as Zn-2(5-bromo-2-pyridilazo)5-diethylaminofenol precipitated complex on the knotted reactor (KR). The limit of detection (0.09 $\mu g\,L^{-1}$ of Zn) of this method makes it particularly suitable for hydrochemical exploration in geological and environmental projects. This application has been validated in the volcanogenic gold (copper, zinc, lead) deposit of La Carolina in the province of San Luis, Argentina. The Carolina Stream and the Grande River have been sampled for water downstream this deposit. The regional background in river water is 2 $\mu g\,L^{-1}$. Six times this concentration has been observed at more than 6.5 km from the source, La Carolina mine.

Keywords: Zinc, Gold, Water, FI-KR-ICP-AES, Hydrochemical exploration, Acid mine drainage

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INTRODUCTION

Zinc is a chalcophile element with peculiar geochemical characteristics that make it of interest, both for prospecting of its own ore deposits and of those deposits where zinc is associated with other elements of economic interest. In base metal and precious metal deposits, zinc is associated with Cu, Pb, Ag, Au, Sb, As, and Se, among others, being an excellent indicator of these ore deposits.[1] For this reason, zinc is used as a pathfinder element in geochemical exploration of many mineral deposits of economic interest, such as those of gold.

The most used exploration methods are based on the analysis of stream sediment, rock, and soil samples and, to a lesser extent, samples of water, vegetation, and gases.

The possibility of applying hydrogeochemical anomalies in geochemical exploration methods, using zinc as a pathfinder element, basically depends, among other factors, on the distance at which these anomalies persist downstream from the mineralized rock until they disappear in the normal interval of background variations. The persistence of zinc hydrogeochemical anomalies depends mainly on the contrast between zinc concentration in the source and the background values, and on the zinc concentration depletion due to dilution or to precipitation barriers.

Many associated elements are found immediately surrounding a specific type of deposit, largely because of the acidic (strongly oxidizing) nature of the water. The closest zones are characterized by high concentrations of a limited number of the more mobile elements, such as Zn, As, Mo, and, sometimes, Hg.[2]

The Zn concentration in the water is due to oxidation of sulphide minerals (pyrite, sphalerite, chalcopyrite, pyrrhotite) before, during, and after mining.[3–6] Thus, Zn often is an element of interest, not only for geological exploration of mineral deposits, but also of environmental concern in relation to the acid mine drainage.

Hydrogeochemical pathfinder elements associated with gold deposits are Ag, As, Se, Pb, Cu, Zn, Ni, and Co in strongly oxidizing media and As, Mo, Zn, and Ag in weakly oxidizing media.[2,7] Among these elements, As is the most commonly used, due to its widespread occurrence in these kinds of deposits.[1,2,8–12] In addition, Zn can be also employed in strongly and weakly oxidizing water and could be an excellent pathfinder for gold deposits.[13] The noncomplexed Zn^{2+} ion dominates at $pH < 8$, while hydrolysis becomes significant at a $pH > 7.5$, especially at low concentrations of carbonate in water.[14,15]

The average concentration of zinc in river water is in the order of 20 $\mu g\ L^{-1}$.[1,2,16,17] In many cases, the Zn concentration is lower than this value and this fact limits, seriously, the use of this element in hydrogeochemical exploration. Therefore, reliable and powerful analytical techniques are required, such as ETAAS (electrothermal atomic absorption spectrometry)

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and ICP-MS (mass spectrometry associated with inductively coupled plasma). ICP-AES (atomic emission spectrometry with inductively coupled plasma) constitutes an interesting alternative and is one of the most widely used techniques for values close to the quantification limit (approximately 40 $\mu g\ L^{-1}$). However, for Zn concentrations below the quantification limit, preconcentration methodologies become necessary. For example, coupling knotted reactors in a continuous flow system is a powerful methodology for this purpose.[18]

With the aim of contributing to the knowledge of hydrochemical behaviour of the Zn, we performed a study of the hydrogeochemical anomalies associated with the epigenetic gold mineralization from the Carolina Mining District in the Grande River basin, in the province of San Luis, Argentina.

AREA DESCRIPTION

La Carolina gold mine is located on the west of the Tomolosta Hill (1.640 meters a.s.l.) in the town of Carolina, 83 km north of San Luis City, Central Argentina (Figure 1). This mine belongs to La Carolina Mining District and is the source of La Carolina stream, a small tributary of the Grande River.

Geologically, this area is situated in the southern block of the Eastern Pampean Ranges. The Palaeozoic metamorphic basement, consisting of

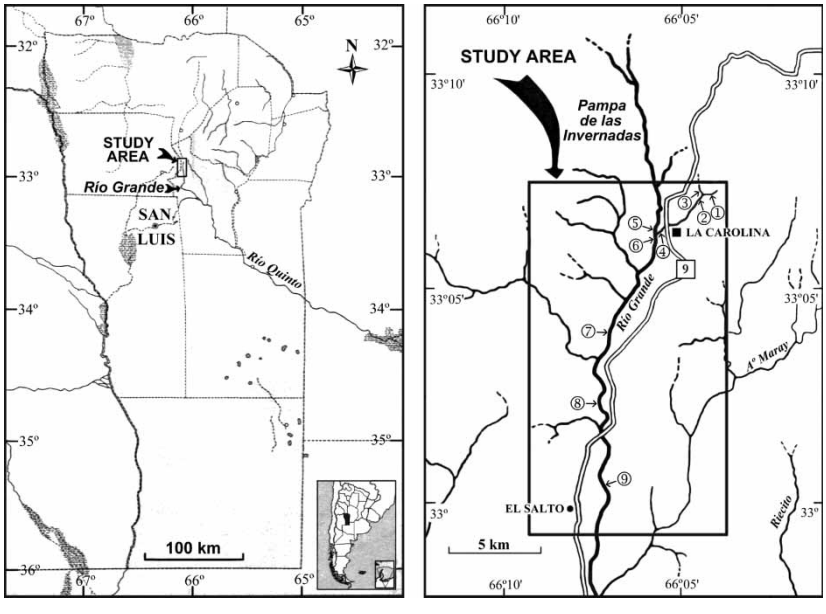

Figure 1. Location of the source of the mine acidic water associated with the gold deposit of La Carolina, San Luis, Argentina, and the rest of the sampling sites.

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phyllitic and quartzitic schists, mica schists, and granitoids, is intruded by a Tertiary andesitic-trachyandesitic complex.[19,20] The epigenetic gold mineralization occurs associated with this complex. Mineralization consists of quartz veins with auriferous pyrite, native gold, chalcopyrite, sphalerite, and galena, accompanied by abundant clay material, product of the alteration of the host rocks.

Genetically, La Carolina gold deposit is related to the andesitic and trachyandesitic rocks of the Tomolasta hill and is constituted of epithermal quartz veins filling fractures concordant with the host schists.[21,22] The gold tenor is very variable, with an average concentration of 4 $\mu g/g$. Currently, no mining activities are being carried out, but several exploratory surveys have been realized in the area, searching for new deposits. This area was an important mining district during the XVIII and XIX centuries.

EXPERIMENTAL

Sampling

Although, in geochemical exploration studies, it is habitual to take a single sample in each sampling site, in our particular case, considering that this is a retrospection study (being the source known, it is proposed the procedure that best fits its identification), we decided to take three samples at each sampling site to check the repeatability of the method and, then, obtain the corresponding mean values.

Immediately after collection, the river water samples were filtered through membrane filters of 0.45 μm pore diameter, acidified to pH 2 with HNO_3, and stored in glass bottles at 4°C within a refrigerator.

Analysis

The pH was determined in the field using a portable pH meter (Orion Research, Inc., Orion 230 A, Beverly, MA, USA) equipped with a 9107 BN Orion glass electrode.

The zinc concentration of river water samples was determined using an on-line system composed of flow injection (FI) and a knotted reactor (KR) associated with inductively coupled plasma atomic emission spectrometry (ICP-AES). The zinc was retained as Zn-2(5-bromo-2-pyridilazo)5-diethylaminofenol precipitated complex on the knotted reactor, following the method described by Salonia et al.[18] The scheme for the collection and preconcentration of Zn in the knotted reactor is shown in Figure 2. The measurements were performed with a sequential ICP-AES spectrometer (Bair, ICP 2070, Beldford, MA, USA).

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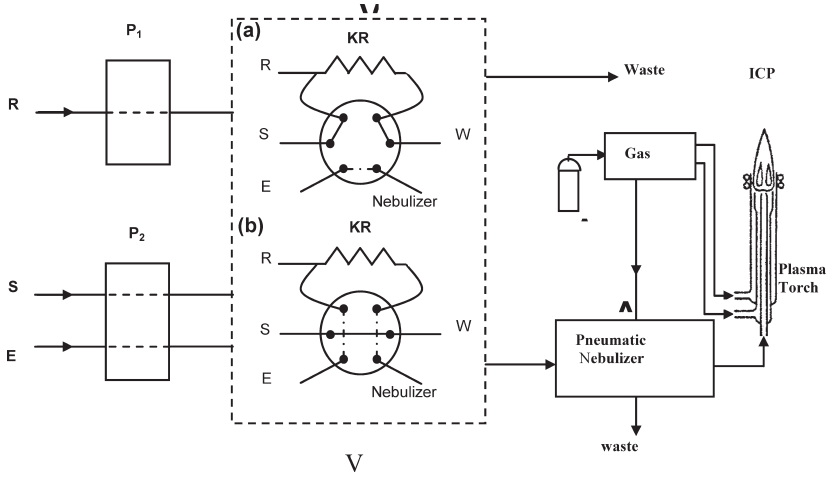

Figure 2. Schematic representation of the FI-KR-ICP-AES system (after Salonia, et al., 2000).[18] P_1 and P_2: peristaltic pump; V: load-injection valve [(a) load position, (b) injection position]; R, reagent; S, sample; E, eluent; W, waste.

RESULTS AND DISCUSSION

Table 1 shows the values for zinc concentration and pH, sampling site, and distance from the source, in water samples collected in February during the rainy season. The sampling sites reported in the table correspond to those in Fig. 1.

The mine acidic water where the samples were collected (sampling site no. 1) have a flow of 50 liters/min and they pour into the Carolina stream. The mean concentration of zinc in the water at this site was 12 mg L^{-1} and the pH was 2.6. Taking as *baseline value* the 2 μg L^{-1} of Zn (pH 7.2) in sampling site no. 5 (Grande River before the input of La Carolina stream) or the 5 μg L^{-1} of Zn (pH 6.5) of sampling site no. 2 (La Carolina stream before the input of mine acidic waters), the difference with respect to sampling site no. 1 is more than three orders of magnitude, which completely meets the contrast requirement between the zinc concentrations in the *source* and the baseline level.

Immediately after the confluence of La Carolina stream with the mine acidic water, the Carolina stream had a mean pH 3.2 and mean Zn concentration of 850 μg L^{-1}. This value remained the same, with only minor variations, up to the confluence of the Carolina stream and Grande River. In the Grande River, which has a flow several times higher than the Carolina stream, a fall in the Zn concentration was to be expected due to the dilution after the confluence. The samples obtained a few meters downstream after this confluence had an average zinc concentration of 75 μg L^{-1} and pH 5.3 (sampling site no. 6). Approximately 3 km downstream of the confluence,

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Table 1. Zinc concentration and pH values, indicating sampling site and distance from source

Sampling site concentration	Distance from the source (km)	pH	Zn ($\mu g\ L^{-1}$)
1-Source: mine acidic water ("La Carolina" mine)	0	2,6	12000
2-Carolina Stream (before its confluence with the mine water)	0,15	6,5	5
3-Carolina Stream (after its confluence with the mine water)	0,5	3,2	850
4-Carolina Stream (before its confluence with Grande river)	1,5	3,5	800
5-Grande river (before its confluence with Carolina Stream)	1,7	7,2	2
6-Grande river (after its confluence with Carolina Stream)	1,9	5,3	75
7-Grande river (downstream from its confluence with Carolina Stream)	4,5	5,6	58
8-Grande river (downstream from its confluence with Carolina Stream)	6,5	6,1	12
9-Grande river (downstream from its confluence with Carolina Stream)	8,5	6,9	2

the average pH increased to 5.6 and the mean zinc concentration diminished to 58 $\mu g\ L^{-1}$ (sampling site no. 7). Five km downstream, the mean zinc concentration was 12 $\mu g\ L^{-1}$ and the average pH was 6.1 (sampling site no. 8). Finally, the samples collected approximately 7 km downstream exhibited mean values of 2 $\mu g\ L^{-1}$ for Zn concentration and pH 6.9. These values remained practically the same further downstream.

The Zn normal contents in river water in the province of San Luis are hardly above 10 $\mu g\ L^{-1}$,[23] with minor differences due to seasonal variations. These concentrations contrast drastically with those found in stream waters related to the gold mineralization of La Carolina gold mine. The similar geological characteristics of other areas of San Luis Province, in particular, and eastern Andes, in general, makes suitable the use of Zn for hydrogeochemical exploration in acid and oxidant environments.

CONCLUSIONS

The results obtained in this work show that the followup of Zn hydrogeochemical anomalies from surface waters constitutes an advantageous sampling system for hydrochemical exploration, due to simplicity of collection and preparation for analysis. Considering that, in many cases, the Zn concentration

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in surface waters is lower than the average content (20 $\mu g\, L^{-1}$), the only additional condition for the use of Zn as mineral deposits pathfinder and environmental proxy is to apply an analytical technique which is fast and sensitive enough for low level Zn concentrations. With this in mind, a FI-KR-ICP-AES system is proposed to monitor weak anomalies, especially in those cases where the pH is close to the Zn hydrolysis (pH $>$ 7.5).

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