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Application of instrumental neutron activation analysis and inductively coupled plasma-mass spectrometry to studying the river pollution in the State of Minas Gerais

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Instrumental neutron activation analysis (INAA) and inductively coupled plasma-mass spectrometry (ICP-MS) have been used for the determination of toxic heavy metals and other pollutants in the water of the Das Velhas river in the State of Minas Gerais, in south-east Brazil. Elemental concentrations of about 60 elements were measured in water samples collected to different parts of this river and from two affluents. There was a good agreement between the two analytical methods and the results were complementary. The results indicated an increase in the concentration of several polluting elements in the water from mining industry area.

Introduction

Several metals are present in rivers and lakes as a result of domestic and industrial human activities: dead and decomposing animals and vegetation, fallout of atmospheric particles and rocks and soils exposed to surface waters. Heavy metals are not biodegradable and enter into the food chain by a number of pathways. The accumulations of Cr, Mn, Co, Cu and other elements in the aquatic environment raise the risk of toxic concentrations of these elements which interfere with a number of life processes.

The state of Minas Gerais is the fourth largest state of Brazil. Its many sources of freshwater provide up to 20% of electricity produced in Brazil. The Das Velhas river of Minas Gerais runs through a region which is rich by Fe, Au and Mn ores and the state itself is the world's second largest producer of minerals. Wastewaters from about 24 legal and several clandestine industries are discharged into the Das Velhas river. In spite of environmental controls carried out by multinational companies, pollution from smaller, sometimes clandestine, industry is still rife. This is the largest environmental problem in Minas Gerais state. Studies of freshwater ecosystems in Minas Gerais are just beginning and ecological problems have been identified in rivers, lakes and reservoirs.[1]

Several methods have been used to measure the environment pollution in water, sediments and aquatic plants, etc. Instrument neutron activation analysis (INAA) is a classic method for multi-elemental determinations which has a high sensitivity at trace level.[2,3] The concentration of metal traces is very reliable in environmental control.[4] This technique has been widely used for the analysis of water and sediment from freshwater.[5–8] Inductive coupled plasma-mass spectrometry (ICP-MS) may also be used for trace analysis of environmental samples. The ICP-MS multi-elemental technique is accurate, sensitive and fast,[9] allowing a daily processing rate of up to 100 samples or more and has recently been used to determine the composition of river water and for routine trace analysis.[10,11] ICP-MS has became one of the preferred methods of elemental analysis with detection limits for most elements less than 0.1 μg/l.[12] In this work INAA and ICP-MS analysis methods have been used to determine trace level concentrations of several elements in water of the Das Velhas river. The sources of potential error in heavy metal analysis were associated with the sampling and subsequent storage of sample prior analysis.[13] This paper studies sampling and storage methods to minimize problems of contamination and losses of metal heavy elements in the water sample and tries to compare the analytical performance of INAA and ICP-MS.

Experimental

Study area and sampling

Water samples were collected near the source of the approx. 100 km long Das Velhas river in January 1995. The Das Velhas river flows into the São Francisco river which in Brazil is known as "The National Integration River" because it runs across four states and it is being used for navigation, recreation and the production of electricity. The sampling areas are indicated in Fig. 1.

Water samples, collected near the river bank at a depth of 15 cm were placed in 125 ml Nalgene bottles and stored at 4 °C. Temperature, pH and electrical conductivity were measured at each sites. We did not detect significative variations of the parameters between the different areas. The average values were: temperature 25 °C; pH 7.2; electrical conductivity 30 μS. The samples were taken in duplicate and half of them were acidified on site with 5 drops of high purity nitric acid (pH ~ 2). This acidification is thought to reduce any absorption on the walls of the bottles.[13–15] We have investigated the particle separation both by filtration and centrifugation. The effect of storage was measured after 3 months.

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Table 1. Concentrations of the elements detected in acidified and non-acidified water samples

Element*	S1		S7	
	Acidified	Non-acidified	Acidified	Non-acidified
(1) Li	0.60 ± 0.06	0.50 ± 0.05	12.0 ± 1.2	2.4 ± 0.2
(1) B	< 2	< 2	7.0 ± 0.7	5.0 ± 0.5
(1) Al	207 ± 20	52 ± 2	–	–
(1) Ca	6650 ± 665	4100 ± 410	84 750 ± 8475	17 300 ± 1730
(1) Ti	5.0 ± 0.5	< 0.3	22 ± 2	5.6 ± 0.6
(1) V	1.20 ± 0.12	< 0.2	5.6 ± 0.6	< 0.2
(2) Cr	4.6 ± 0.2	< 0.8	15.0 ± 1.5	< 0.8
(2) Co	0.50 ± 0.05	< 0.04	63 ± 6	1.50 ± 0.02
(1) Ni	1.3 ± 0.4	0.80 ± 0.08	47.5 ± 4.8	4.0 ± 0.4
(1) Cu	0.8 ± 0.2	0.30 ± 0.09	41 ± 4	0.9 ± 0.1
(2) Zn	< 24	< 24	80 ± 15	< 24
(1) Ga	0.10 ± 0.01	< 0.02	9.1 ± 0.9	3.5 ± 0.4
(2) As	0.30 ± 0.03	0.40 ± 0.12	2.3	0.35 ± 0.04
(1) Se	< 0.7	< 0.7	< 0.7	< 0.7
(1) Rb	2.2 ± 0.2	2.1 ± 0.2	6.4 ± 0.6	2.70 ± 0.03
(1) Sr	7.7 ± 0.7	8.9 ± 0.9	115 ± 12	82 ± 8
(1) Y	0.13 ± 0.03	< 0.02	35 ± 4	0.14 ± 0.01
(1) Zr	0.13 ± 0.03	< 0.16	1.3 ± 0.04	< 0.16
(1) Nb	< 0.02	< 0.02	< 0.02	< 0.02
(1) Mo	< 0.07	< 0.12	< 0.07	< 0.12
(1) Cd	< 0.10	< 0.10	0.3 ± 0.1	< 0.10
(1) Sn	< 0.06	< 0.06	< 0.05	< 0.05
(2) Sb	< 0.05	< 0.11	0.06 ± 0.02	< 0.11
(1) Te	< 0.60	< 0.60	< 0.50	< 0.60
(1) Cs	0.10 ± 0.01	0.08 ± 0.01	0.40 ± 0.05	0.04 ± 0.01
(2) Ba	8.60 ± 0.86	10 ± 1	378 ± 38	162 ± 16
(2) La	0.19 ± 0.02	< 0.06	65 ± 7	0.26 ± 0.03
(2) Ce	0.93 ± 0.09	< 0.13	115 ± 12	0.57 ± 0.06
(1) Hf	< 0.04	< 0.04	< 0.04	< 0.04
(1) Ta	< 0.01	< 0.01	< 0.01	< 0.01
(2) W	< 0.1	< 0.3	< 8	< 0.3
(1) Pt	< 0.06	< 0.06	< 0.06	< 0.06
(2) Au	< 0.01	< 0.01	0.05 ± 0.01	< 0.01
(1) Tl	< 0.08	< 0.08	0.40 ± 0.04	< 0.08
(1) Pb	< 1.50	< 1.5	45.0 ± 4.5	< 1.5
(1) Bi	< 0.02	< 0.02	< 0.02	< 0.02
(1) Th	< 0.02	< 0.02	1.3 ± 0.1	< 0.02
(2) U	< 0.03	< 0.03	6.0 ± 0.6	< 0.03

*Analytical method retained: 1 – ICP-MS; 2 – INAA.

Instrumental neutron activation analysis (INAA)

Water samples must be pre-concentrated before irradiation in order to perform neutron activation analysis. 10 ml sample were evaporated in high purity quartz ampoules, Suprasil, 80 °C for 10 days and heat-sealed. The samples and standards were irradiated in Saclay's OSIRIS nuclear reactor at a neutron flux of $1.4 \cdot 10^{14}$ $n \cdot cm^{-2} \cdot s^{-1}$ for 17 hours. The γ-rays subsequently emitted were counted for 8 hours, after a decay time of 10 and 20 days, with a 100 cm^3 coaxial HpGe PGT detector coupled to a 4096 pulse-height analyzer. The computational K_0 method[16] was used to determine the concentration of elements of interest.

Inductively coupled plasma spectrometry

ICP-MS measurements were carried out using the multi-element modes. An analytical program was established for both calibration and routine analysis. This program uses a series of automated operations to align the optics, select the analytical wavelength for the peaks and position the source on the entrance slit in order to optimize the signal. The selected analytical wavelenghts are the characteristics lines of the elements, which are free from spectral interference. This avoids the need for corrections at concentration level of interest. The ICP-MS used in this study was a PQ 2-Plasma Quad with a Meinhard ultrasonic nebulizer.

The data acquisition was controlled using PQ VISION software. The measurements were taken in duplicate, using the following operating conditions: ICP-MS r.f. power: 1.35 K; coolant argon flow: 14 l/min; nebulizer argon flow: 0.8 l/min; auxiliary argon flow: 0.8 l/min; sample uptake rate: 0.6–1 ml/min. The instrument was calibrated with a commercial solutions (SPEX) which contained standards prepared out of 10 ppb multi-elementary and 1000 ppb Ca solutions. Blanks were also used in order to enable an accuracy of 2–3%. The internal standards of samples were 10 ppb solution of In, Re, Be.

Table 2. Concentration of metals in ultrapure water (in ppb)

Element	Non-treated	Filtered	Centrifuged
Ni	< 0.2	2.0 ± 0.2	< 0.2
Cu	< 0.1	2.0 ± 0.2	< 0.1
Zn	< 4	15 ± 2	< 2
Ag	< 0.03	12 ± 2	< 0.03
Cd	< 0.1	0.30 ± 0.03	< 0.2
Sn	< 0.05	0.30 ± 0.03	< 0.05
Sb	< 0.03	0.40 ± 0.04	< 0.03
Pb	< 0.15	12 ± 1	< 0.15

Analytical method: ICP-MS.

Table 3. Detection limits for the determination of elements in liquid solutions (in ppb)

Element	INAA	ICP-MS	Element	INAA	ICP-MS	Element	INAA	ICP-MS
Li	*	**0.1**	Sr	4	**0.2**	Gd	*	**0.03**
Be	*	**0.01**	Y	*	**0.01**	Tb	**0.006**	**0.01**
Na	**11**	**	Zr	**5**	**0.05**	Dy	–	**0.02**
Mg	*	**0.2**	Nb	*	**0.01**	Ho	*	**0.01**
Al	–	**0.3**	Mo	**0.12**	0.12	Er	*	**0.02**
Ca	100	**40**	Ru	**0.01**	0.03	Tm	*	**0.01**
Sc	**0.002**	0.25	Rh	*	**0.01**	Yb	**0.002**	0.02
Ti	–	**0.2**	Pd	–	**0.001**	Lu	**0.0004**	0.01
V	–	**0.2**	Ag	0.03	**0.04**	Hf	**0.006**	0.03
Cr	**0.8**	0.7	Cd	0.1	**0.1**	Ta	**0.005**	0.01
Fe	**6**	**	Sn	1	**0.05**	W	**0.02**	0.04
Mn	**11**	**	Sb	**0.02**	0.02	Re	–	**0.04**
Co	**0.04**	0.01	Te	*	**0.3**	Ir	**0.0001**	0.02
Ni	**0.1**	**0.6**	Cs	**0.01**	**0.02**	Pt	1	**0.05**
Cu	*	**0.25**	Ba	3	**0.2**	Au	**0.01**	**0.03**
Zn	**24**	2**	La	**0.03**	**0.01**	Hg	**0.02**	0.7
Ga	–	**0.02**	Ce	**0.05**	**0.01**	Tl	*	**0.06**
Ge	–	**0.1**	Pr	*	**0.01**	Pb	*	**0.15**
As	**0.01**	0.23	Nd	**0.1**	**0.03**	Bi	*	**0.02**
Se	**0.06**	0.7	Sm	**0.02**	0.03	Th	**0.004**	**0.02**
Rb	**0.3**	**0.02**	Eu	**0.003**	0.01	U	**0.007**	**0.02**

*Element which is difficult to determine by INAA.
**Element which is difficult to determine by ICP-MS.

Results and discussion

The analysis results of two samples S1 and S7, acidified and non-acidified are shown in Table 1. The sampling area S1 is located in non-polluted region near of the Das Velhas river source and S7 is located in the mining area. The results show highly significant differences in element concentrations between acidified and non-acidified water even more so in water samples S7. Several elements absorbed on suspended matter are released by the acidification process. Sometimes, results for a non-polluted water (S1) certain elements, such as alcalines, are very close in acidified and non-acidified samples. The difference grows for all elements when the water is more fully with particles. This prooves that, even for elements which are reputably soluble in water, a non-negligeable part maybe absorbed by the matter in suspension. Results from our study also indicated that the concentration of elements in water samples remained unchanged after three months of storage.

The separation of suspended matter by filtration process allowed us to distinguish between the elements associated with particular material in suspension and the elements in solution.[10] The drawback with this process is that, unless the filter is washed properly before filtration is carried out, there is a risk of introducing contamination.[15] The preliminary test by filtration of ultrapure water through 0.2 μm Millipore filter revealed a highly significant source of contamination by certain elements such as Ni, Cu, Zn, Ag, Cd, Sn, Sb and Pb. Washing the filters several times with acid followed by several rinses did not proove conclusive. So, in order to avoid all risks we did not carry out any filtration in field, for this first experiment.

A test using a centrifugation process revealed no pollution of the heavy metals before or after centrifugation. The effectiveness of the centrifugation process is a function of the centrifuge speed, time and particle density.

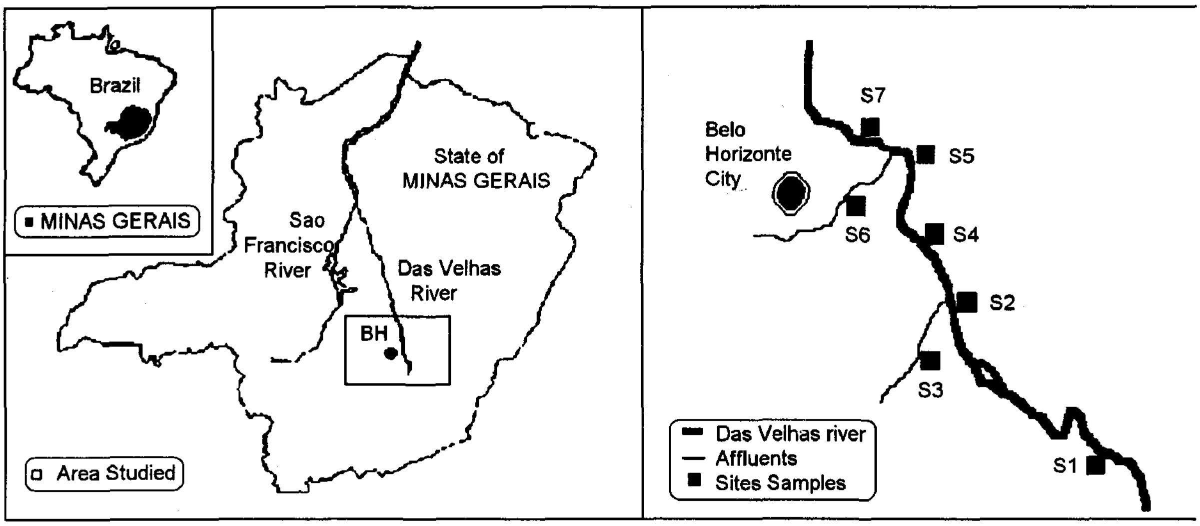

Fig. 1. Location of study area and samples sites in the Das Velhas river and two affluents

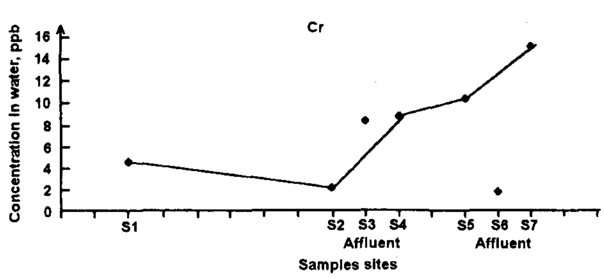

Fig. 2. Concentration of Cr in acidified water samples of the Das Velhas river

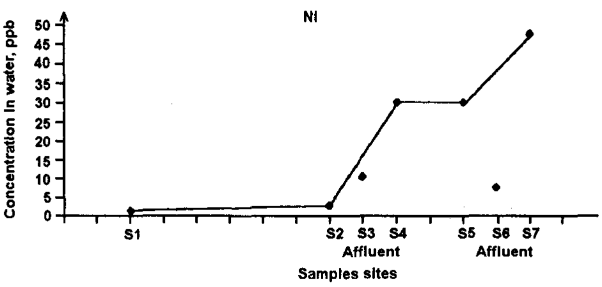

Fig. 4. Concentration of Ni in acidified water samples of the Das Velhas river

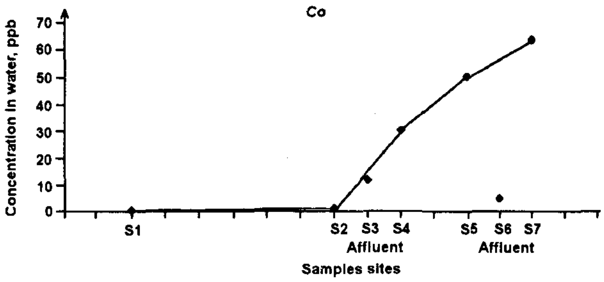

Fig. 3. Concentration of Co in acidified water samples of the Das Velhas river

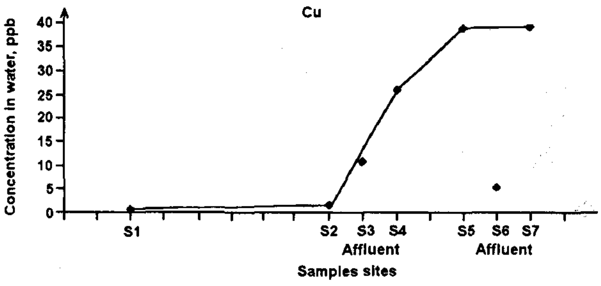

Fig. 5. Concentration of Cu in acidified water samples of the Das Velhas river

A centrifugation at 4300 rpm during 10 minutes removes all suspended material. The comparative data between filtration and centrifugation process is shown in Table 2.

The INAA and ICP-MS detection limits for liquid solutions achieved in our analysis are indicated in Table 3. A blank quartz ampoule irradiated along with water samples is given as limits for INAA method. For ICP-MS the limits obtained are practically identical in the water samples which make up the introduced blanks. Bold numbers in Table 3 represent the most accurate method for each element in our analysis. The two analytical methods are complementary and the concentration of about 60 elements can be determined. Some elements such as Fe and Mn are difficult to dose using ICP-MS because of the interferences series. Other problems revealed by INAA as Pb and Bi, which do not have required sensibility to neutron activation and Al, Ti and V that have a short half-life and cannot be determined during the multi-elemental analysis.

Table 4 shows the results obtained with S1 and S7 samples when it is possible to analyse those elements using both methods. In general results shown agree well.

Some examples: Cr, Co, Ni, Cu, Au, Pb, studied along the course of the Das Velhas river in acidified water samples are showed in Figs 2 to 7. The increase in concentrations of elements towards, S3, which is the beginning of the industrial mining area, confirms a significant source of pollution along the course of the river. This pollution is visible because all the metallic elements correlated to the increase of suspended matter. However, compared to this general situation we noticed that certain elements behaved abnormally. High concentration of Cr, confirmed by a second analysis, maybe due to a domestique leather treatment in S1 and S2 areas. The abrupt rise in concentration of Au in water sample S6 is justified from the high exploitation of Au in this region of affluent. The same increase of As concentration is demonstrated in S6 perhaps due to an old arsenic mine, abandoned some 20 years ago.

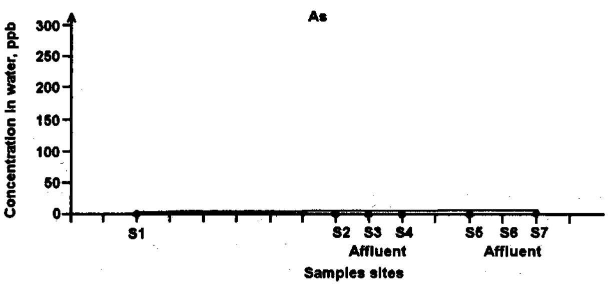

Fig. 6. Concentration of As in acidified water samples of the Das Velhas river

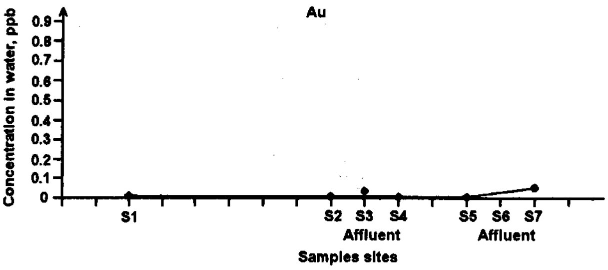

Fig. 7. Concentration of Au in acidified water samples of the Das Velhas river

Conclusions

The association of INAA and ICP-MS for multi-elementary analysis, allows the investigation of about 60 elements in water samples. The methods are complementary and are able to confirm the concentration of pollutants from industrial mining in rivers.

This study was developed in order to analyse the sediments and water samples taken in the field by filtration after making sure that the filtration is not polluted. It will be possible to use the analytical methods which have been perfected on these new samples. Complete analysis of sediments are required for full interpretation of river pollution. INAA and ICP-MS can be used for these analyses. However, the sediments must be in total solution before analysis with ICP-MS.

Table 4. Results comparing INAA and ICP-MS analysis in S1 and S7 acidified water samples (in ppb)

Element	S1		S7	
	INAA	ICP-MS	INAA	ICP-MS
Cr	4.6 ± 0.2	2.0 ± 2.5	15.0 ± 1.5	16.0 ± 2.5
Co	0.50 ± 0.05	0.70 ± 0.20	63 ± 6	78 ± 12
As	0.30 ± 0.03	0.46 ± 0.20	2.3 ± 0.2	1.5 ± 0.5
Rb	1.7 ± 0.3	2.2 ± 0.2	7 ± 2	6.4 ± 0.6
Ag	< 0.08	< 0.04	< 0.4	< 0.04
Sb	< 0.05	0.05 ± 0.01	0.06 ± 0.02	0.04 ± 0.01
Cs	0.09 ± 0.02	0.10 ± 0.01	0.30 ± 0.05	0.40 ± 0.05
Ba	8.60 ± 0.86	10 ± 2	378 ± 38	270 ± 40
Hf	< 0.02	< 0.04	< 0.08	< 0.04
Au	< 0.01	< 0.03	0.05 ± 0.01	0.06 ± 0.02
Th	0.012 ± 0.007	< 0.02	1.3 ± 0.1	1.4 ± 0.3
U	< 0.03	< 0.02	6.0 ± 0.6	5.6 ± 0.4
La	0.19 ± 0.02	0.18 ± 0.02	65 ± 7	62 ± 10
Ce	0.93 ± 0.09	0.95 ± 0.15	115 ± 12	110 ± 11
Nd	< 1.1	0.17 ± 0.02	52 ± 5	60 ± 6
Sm	0.04 ± 0.01	0.04 ± 0.02	15 ± 2	12 ± 2
Eu	0.006 ± 0.003	< 0.02	1.7 ± 0.5	2.8 ± 0.4
Yb	0.010 ± 0.005	< 0.02	2.7 ± 0.3	3.0 ± 0.3
Lu	≤ 0.002	< 0.01	0.40 ± 0.04	0.40 ± 0.04

*

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