

Simultaneous Determination of Trace Elements in Tinishu Akaki River Water Sample, Ethiopia, by ICP-MS

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Résumé

La spectrométrie de masse à plasma à couplage inductif (ICP-MS) fut employée pour la détermination simultanée de 8 métaux lourds dans des échantillons d'eau prélevés de la rivière Tinishu Akaki, en Ethiopie, et de ses effluents durant la période de décembre 2002 à janvier 2003, pour la première campagne, et de novembre 2003 à janvier 2004, pour la seconde campagne. La justesse fut évaluée au moyen de l'analyse de matériaux de référence certifiés. Les différences entre les valeurs mesurées et certifiées pour SLRS-4, BCR 713 et BCR 714 étaient moins de $\pm 9\%$, dans la plupart des cas. Les concentrations de 7 ou 8 des 8 éléments déterminés étaient statistiquement indistingables des valeurs certifiées. La précision d'ICP-MS était généralement meilleure que 5 % d'écart-type relatif. Les limites de détection pour la plupart des éléments allaient de 0.001 à 0.01 $\mu\text{g L}^{-1}$. Excepté pour le Cr and le Mn, les concentrations élémentaires mesurées dans les échantillons d'eau de la rivière Tinishu Akaki satisfont les standards de qualité d'eau de surface de classe 2 - 4; cette eau peut donc être employée à l'irrigation.

Abstract

Inductively coupled plasma mass spectrometry was used for the simultaneous determination of 8 heavy metals in water samples collected from Tinishu Akaki

River, Ethiopia, and its tributaries during the period December 2002 to January 2003 (first campaign) and November 2003 to January 2004 (second campaign). Accuracy was evaluated by analysis of certified reference materials. The differences between measured and certified values in SLRS-4, BCR 713 and BCR 714 were less than $\pm 9\%$ in most cases. The concentrations of 7 or 8 out of the 8 elements determined were statistically indistinguishable from the certified values. The ICP-MS precision was usually better than 5 % RSD. The limits of detection for most elements ranged from 0.001 to 0.01 $\mu\text{g L}^{-1}$. The elemental concentrations measured, except for Cr and Mn, in Tinishu Akaki River water samples fulfill the surface water quality standard of class 2 - 4, and thus the water can be used for irrigation.

Keywords: ICP-MS, trace elements, river water, Tinishu Akaki, Ethiopia.

Introduction

The importance of environmental quality in Ethiopia, generally, and in and around Addis Ababa, the capital of Ethiopia, in particular has recently attracted a great deal of interest.

Industrial units located in and at the outskirts of the city, intensive agricultural practices along the riversides and indiscriminate disposal of domestic and municipal wastes are the major sources of Tinishu Akaki River (TAR) water pollution. Exposure to these wastes, which contain toxic components such as heavy metal ions, is of great concern, as it poses not only health risks to humans but also potentially unacceptable ecological risks to plants,

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animals and microorganisms (1).

The accurate determination of trace elements in a variety of environmental samples has received considerable attention in the battle against environmental pollution (2). For the determination of trace elements, various methods have been used, including Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (3), Electro-thermal Atomic Absorption Spectrometry (4), Instrumental Neutron Activation Analysis (5), Total Reflection X-Ray Fluorescence Spectrometry (6) and Hydride Generation Atomic Fluorescence Spectroscopy (7).

ICP-MS has proved to be a powerful and very useful technique for the simultaneous determination of trace elements, and it can thus be of particular importance for fast screening of metal profiles in environmental water at low concentrations and for a wide range of other matrices (1,8,9). It also offers exceptional sensitivity (10) and excellent detection limits (11-14). The analytical capability of ICP-MS in the field of trace element analysis in water has led to considerations of the technique for routine water analysis. Thus, for example, the USEPA (United States Environmental Protection Agency) Method 200.8 uses ICP-MS to test for many trace elements in water (15).

Highly saline solutions, however, can cause some problems, such as clogging of the sampling orifice as well as spectroscopic and non-spectroscopic interferences (9,16,17). Sample dilution, in general, is a possible method to alleviate matrix effects (16). In this work, ICP-MS was used for the simultaneous determination of eight elements after 2- or 50-fold dilution.

The principal objective of the present study is to investigate the input and distribution of trace elements and examine the pollution levels of Tinshu Akaki River with respect to the most important heavy metals, namely Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn.

Study area

Geography

Addis Ababa, the capital city of Ethiopia, is located in the heart of the country. It is the country's commercial, manufacturing, and cultural center. Cement, leather and beverage production are amongst the industrial activities in the city. Addis Ababa has grown at an astonishing speed since it was established in 1886. Today, it has a population of more than three million in a land area of 540 sq km, of

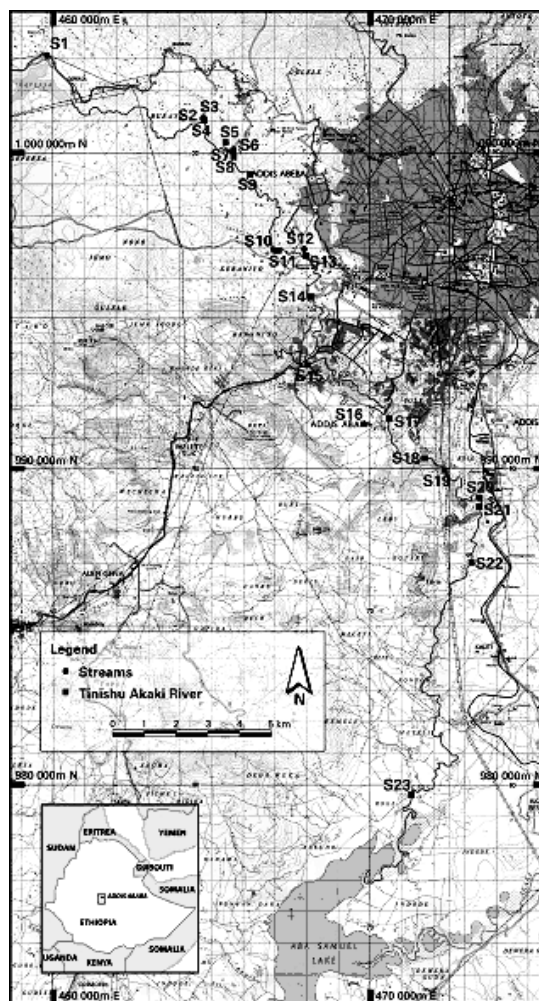


Figure 1. Location of sampling sites in Tinshu Akaki River and its tributaries, Ethiopia

which 18.2 are rural. It lies between 2200 and 2500 meters above sea level on the Central Ethiopian Plateau. Geographically, it is located at 9°N and 38°E. The city rambles pleasantly across many wooden hillsides, and gullies cut through with fast flowing streams, especially during the rainy season from July to September (18). Tinshu Akaki river basin covers the Western part of the city (Figure 1). Geologically, Addis Ababa lies on volcanic rocks ranging in composition from rhyolitic to basaltic types. The main stratigraphic units are constituted by basaltic, rhyolitic, trachytic and trachy-basaltic lava flows and welded tuffs found at different localities and ages (19).

Climate

Despite its proximity to the equator, Addis Ababa enjoys a mild, Afro-Alpine temperate and warm temperate

Table 1. ICP-MS operating conditions

RF power (W)	1000
Plasma argon, L min ⁻¹	15
Nebulizer flow, L min ⁻¹	0.9 - 1
Nebulizer	Cross flow
Data	Peak hop transit
Resolution	Normal
Dwell time (ms)	50
Number of replicates	3
Calibration mode	External calibration

climate. The lowest and the highest annual average temperature are between 10 and 25°C. April and May are the driest months. The main rainy season occurs between mid-June and mid-September; this season is responsible for 70% of the annual average rainfall of 1400 mm. It is characterized by intense rainfall of short duration. During the dry season, the days are pleasantly warm and the nights cool; in the rainy season, both days and nights are cool (20).

Experimental

Instrumentation

1. ICP-MS

The instrument used was a Perkin Elmer Sciex Elan 5000 ICP-mass spectrometer (Perkin-Elmer, Überlingen, Germany) equipped with quartz torch, nickel sampler and skimmer cones, a peristaltic pump (maintaining a 1 mL min⁻¹ sample uptake rate), a cross-flow type pneumatic nebulizer and a double pass Scott-type spray chamber. Operating conditions are summarized in Table 1.

2. Microwave digestion system

For the dissolution of samples, a microwave digestion system (MLS-1200 MEGA, Milestone, USA) with MDR (Microwave Digestion Rotors) technology was used with TFM (Tetrafluormethaxil) vessels.

Reagents and standard solutions

All reagents were of analytical-reagent grade, unless stated otherwise. Water was doubly distilled and further purified using a Milli-Q water purification system (Millipore, USA). Nitric acid was purified by sub-boiling

distillation in quartz equipment. Analytical multi-element standard solutions were prepared by diluting single and multi-element standard solutions (Merck) containing 1 g L⁻¹ metal ions for ICP-MS. A stock internal standard solution containing 10 µg mL⁻¹ of each of In, Sc and Tl was prepared from single-element standard solutions (1000 µg mL⁻¹) for ICP-MS. Where necessary, standards and samples were diluted with 0.14 M HNO₃.

Certified reference material

Certified reference materials for trace elements in riverine water (SLRS-4) and wastewater (BCR 713 and BCR 714) obtained from the National Research Council Canada and Institute for Reference Materials and Measurements (IRMM), Geel, Belgium, respectively, were used to evaluate the accuracy of the proposed method for trace element determination.

Sampling and pretreatment of samples

A short-term field survey of Tinishu Akaki River was carried out in order to locate the important sources of pollution. The study area and the location of sampling stations are shown in Figure 1. Stations for the collection of river water samples included locations along some of the tributaries that enter the river, as well as the main stem of the river. Samples of river water from twenty-three sampling stations along the Tinishu Akaki River and its tributaries were collected during the period between December 2002 and January 2003 (first campaign) and between November 2003 and January 2004 (second campaign). At each sampling location, about 1 liter of water sample was taken from the upper 50 cm (21) surface of the river using polyethylene buckets that had been pre-cleaned and rinsed with water samples. The samples were then transferred to polyethylene bottles. Shortly after sampling, the water samples were filtered using 0.45 µm pore-size membrane filters (NALG, Belgium). Filtered samples were collected in pre-cleaned, high-density polyethylene bottles and acidified to pH < 2 with concentrated nitric acid (Merck, Belgium). Storage and treatment procedures of water samples were described elsewhere by Bartram and Balance (22). Finally, the preserved samples were transported to the Laboratory of Analytical Chemistry, Belgium. For each sample, the concentrations of eight elements were measured by ICP-MS. The isotopes monitored were ¹¹⁴Cd, ⁵⁹Co, ⁵²Cr, ⁶³Cu, ⁵⁵Mn, ⁶⁰Ni, ²⁰⁸Pb and ⁶⁶Zn. These isotopes are believed to be either free from polyatomic

interferences or the effects of these interferences are usually negligible in water samples. The 8 elements were chosen for analysis taking into consideration existing analytical expertise and the history of human activity in Tinishu Akaki River.

Physicochemical parameters, major ions and nutrients

During each sampling period, corresponding values of pH, temperature, electrical conductivity, dissolved oxygen and total dissolved solids (TDS) were measured *in situ* using X-mate^{pro} portable meters and their various interchangeable sensors (Mettler Toledo, Switzerland). Further samples were collected for the determination of major ions and nutrients such as calcium, magnesium, nitrate, nitrite, ammonia, sulfate, phosphate, bicarbonate and chloride. The analyses of major ions and nutrients were performed as described elsewhere (23).

Analytical procedure for trace element analysis by ICP-MS

Ion lens voltages of the instrument and the plasma operating conditions, such as the nebulizer flow rate, the position of the torch and RF power, were optimized while continuously nebulizing a 50 ppb multi-element standard solution of Be, Co, Rh, In, Pb and Tl so as to maximize the ¹⁰³Rh and ¹¹⁵In signals. The ion lens voltages were chosen each time the sampler and skimmer were replaced and/or cleaned. The plasma operating conditions were selected to obtain a good compromise between high sensitivity and low oxide levels.

Calibration

External calibration was accomplished by using a blank and a standard solution with the 8 trace elements, the concentration of which was close to that estimated for the analyte considered. The matrix of the blank and the standard solution was 0.14 M HNO₃. The following analysis sequence was applied: first the blank, then several samples and, only at the end of the sequence, the standard. The blank intensity was subtracted from both the standard and the sample intensities. When standard addition was applied, each analysis was done by using the intensities obtained by subtracting the blank intensity from that of the unspiked and spiked solutions. Internal standards were always used to allow a correction for intensity drift.

For ICPMS measurements, 0.2-5 mL of sample was

pipetted into a 10 mL polyethylene tube. Then 50 µL of 10 mg L⁻¹ Sc, In and Tl was added as internal standard, and the volume was adjusted to 10 mL with 0.14 M HNO₃. Blank and 100 µg L⁻¹ multi-element standard measurements were carried out, as well.

Microwave digestion

To reduce matrix effects and clogging of the skimmer, samples may be digested before analysis. To test the need for a laborious sample digestion, one reference material was analysed with and without microwave digestion. 50 mL of Riverine water reference material (SLRS-4) was introduced directly into the digestion vessel, and 3 mL of concentrated HNO₃ and 2 mL of 28% H₂O₂ (Merck Euro lab, Belgium) were added. The sealed vessels were placed inside a rotor of the microwave digestion system and submitted to a microwave dissolution program (24): 2 min at 200 W, 10 min at 800 W, 10 min at 250 W and 5 min vent at zero W. Appropriate batch blanks were prepared with each set of samples. After cooling, the digest was transferred to a graduated flask.

Results and Discussion

Optimization of analytical procedure: internal standard and calibration method

1. Choice of internal standard

A number of studies have investigated the analysis of trace elements in water samples (7,25). These studies have typically combined a careful choice of internal standard with dilution to minimize matrix-induced signal suppression or enhancement and to compensate for signal drift and for instrumental instability. Sample dilution is believed to be necessary to avoid rapid blockage of the torch and of the pneumatic nebulizer and to reduce the extent of signal suppression due to the matrix.

In order to obtain accurate results, the internal standard should closely match the analyte in terms of mass number and ionization potential, as cited in previous work by Moens and Dams (26), amongst others. This is clearly confirmed by the results obtained in this work.

Since the analyte elements are spread over a wide range of atomic masses, three internal standards, Sc, In and Tl, were selected for Co, Cr, Cu, Mn, Ni and Zn; Cd; and Pb, respectively. Accurate and precise values were obtained for the certified reference materials SLRS-4, BCR 713 and BCR 714 using the internal

Table 2. Analysis of SLRS-4 Riverine water reference material by external calibration and by standard addition, after simple dilution and after microwave digestion.

Isotope analysed	Concentration ($\mu\text{g L}^{-1}$), 95 % C.I., (n = 4)						
	Certified values	External Calibration	% Deviation	Standard Addition	% Deviation	After microwave digestion	% Deviation
^{114}Cd	0.012 \pm 0.002	0.013 \pm 0.003	8.3	0.013 \pm 0.004	8.3	0.012 \pm 0.001	0
^{59}Co	0.033 \pm 0.006	0.034 \pm 0.001	3	0.035 \pm 0.013	6.1	0.032 \pm 0.001	-3
^{52}Cr	0.33 \pm 0.02	0.34 \pm 0.01	3	0.34 \pm 0.12	3	0.32 \pm 0.01	-3
^{63}Cu	1.81 \pm 0.08	1.9 \pm 0.1	6.6	1.9 \pm 0.7	7.2	1.8 \pm 0.1	-2.2
^{55}Mn	3.37 \pm 0.18	3.5 \pm 0.1	3.3	3.5 \pm 1.2	5.3	3.4 \pm 0.1	0.6
^{60}Ni	0.67 \pm 0.08	0.80 \pm 0.16	19	0.8 \pm 0.3	20.9	0.8 \pm 0.2	16
^{208}Pb	0.086 \pm 0.007	0.061 \pm 0.004	-29	0.06 \pm 0.03	-29	0.05 \pm 0.04	-41
^{66}Zn	0.93 \pm 0.1	0.93 \pm 0.15	0	0.9 \pm 0.3	-7.5	0.92 \pm 0.02	-1.1

Table 3. Analysis of wastewater reference materials by standard addition

Isotope analysed	Concentration ($\mu\text{g L}^{-1}$), 95 % C.I., (n = 3)					
	BCR 713, Effluent Wastewater			BCR 714, Influent wastewater		
	Result	Certified value	% Deviation	Result	Certified value	% Deviation
^{114}Cd	5.2 \pm 0.4	5.1 \pm 0.4	1.9	17.4 \pm 2.7	19.9 \pm 1.6	-12.5
^{52}Cr	22.15 \pm 1.4	21.9 \pm 2.4	1.1	121 \pm 12	123 \pm 10	-1.6
^{63}Cu	69 \pm 7	69 \pm 4	0	329 \pm 21	309 \pm 23	6.5
^{55}Mn	44.7 \pm 3.6	43.4 \pm 3.0	3	96 \pm 7	103 \pm 10	-6.8
^{60}Ni	31 \pm 2	30 \pm 5	3.3	112 \pm 14	108 \pm 15	3.7
^{208}Pb	47 \pm 3	47 \pm 4	0	143 \pm 13	145 \pm 11	-1.3
$^{66}\text{Zn}^*$	0.19 \pm 0.03	0.22 \pm 0.04	-13.6	3.20 \pm 1.38	1.00 \pm 0.10	220

* Values in mg L^{-1}

standards mentioned above.

2. Calibration methods

In addition to internal standardization, three calibration methods can be used in ICP-MS, namely, external calibration, standard addition and isotope dilution methods. Two of the three calibration methods, external calibration and standard addition, were investigated in this work. Standard addition is widely known for improving the accuracy in the presence of a heavy matrix (27). In many cases, external calibration is sufficient, on the condition that an appropriate internal standard is chosen that may also correct for multiplicative matrix effects. As shown in table 2, both methods yielded comparable results with

a comparable precision; the less time-consuming external calibration method was thus used for further analyses (25).

The digestion of water samples with $\text{HNO}_3/\text{H}_2\text{O}_2$ demonstrated good recoveries of almost all trace elements in the CRM of riverine water origin (Tables 2 and 3). However, the microwave digestion procedure is laborious and susceptible to contamination. Therefore, the rest of the analyses were conducted following external calibration after simple dilution of samples.

Validation

In order to validate the procedure for its accuracy, the optimized analytical procedures were applied to

various certified materials: riverine water (SLRS-4) and wastewater (BCR 713 and BCR 714). The results obtained by using the two different calibration methods are summarized in Tables 2 and 3, together with the certified values, for the determinations done after simple dilution and after microwave digestion. Working with smaller dilution factors (2-fold) for SLRS-4 would also help to elevate ICP-MS signals of Cd and Pb above measured blank levels. The microwave digestion method for SLRS-4 was performed using the external calibration technique. From these results, it appears that microwave digestion is not required for pristine water samples.

The ICP-MS precision was usually better than 5 % RSD (it deteriorated up to 13 and 11.8 % for Cd and Zn in SLRS-4, respectively). In the case of the microwave digestion method, the precision was better than 9% except for Pb, which had a precision of 16.6 % RSD. For wastewater reference materials, the precision was better than 5 % RSD and 9 % RSD for BCR 713 and BCR 714 (except Zn, 23.4%), respectively. The Zn value for BCR-714 was obviously too high owing to strong spectroscopic interferences.

When the accuracy is evaluated by comparing the results with the certified values of reference materials, nearly all measured values agree within the 95 % confidence interval. The differences between measured and certified values in SLRS-4, BCR 713 and BCR 714 are usually less than ± 9 %; however, the accuracy for Ni and Pb in SLRS-4 is poor (± 16 -21, 29-41 %, respectively, Table 2). The accuracy for Zn in BCR 713 and Cd in BCR 714 was deteriorated, with deviations of 13.6% and even a factor of 3.2 (Table 3). Zn has been identified as a difficult element to measure accurately in BCR 714, influent wastewater of high concentration. The precision obtained was very low, but probably a strong unidentified spectroscopic interference was also present. It can be concluded that, for this determination, application of a chemical separation or the use of a higher resolution ICP-MS is required.

The method of standard addition, in general, provides more accurate results than external calibration, as it compensates for ionization interferences.

Detection limits

Limits of detection were estimated as the concentrations corresponding to three times the standard deviation, σ , of the intensities of the blank signals at the m/z of each analyte. A 0.14 M nitric acid solution was

Table 4. Detection Limit ($\mu\text{g L}^{-1}$) of the procedure

Element	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
DL	0.001	0.001	0.010	0.002	0.002	0.004	0.005	0.031

used as a blank, and the limits of detection are summarized in Table 4. The average values and the standard deviation of the blank signals were obtained by using the results of 10 replicate measurements of 0.14 M nitric acid and 5 measurements of 100 $\mu\text{g L}^{-1}$ standard. The limits of detections for most elements ranged from 0.001 to 0.01 $\mu\text{g L}^{-1}$.

Analysis of Tinshu Akaki River (TAR) water samples

The optimized method was applied for the analysis of Tinshu Akaki River water samples following the external calibration procedure after simple dilution, as previously described for certified reference materials of riverine water.

Table 5 shows that 8 elements could be determined simultaneously after 2- or 50-fold dilution of TAR water. The 2-fold dilution was applied to all elements except Mn. A dilution factor of 50 was used for manganese, especially for water samples taken from S9 – S23, in order to avoid signals that were too high for the detector to measure adequately.

The relative standard deviation was less than 5% for most of the elements, but sometimes deteriorated to 19 % for Cd and Pb, as their concentration is low in the water samples. However, natural waters are more complex in chemical composition than the reference materials. The main chemical composition of waters considered in this study showed a range of pH (7.2 - 8.9), TDS (28 - 639 mg L^{-1}), Ca (19 - 67 mg L^{-1}), Mg (3 - 32 mg L^{-1}), bicarbonate (87 - 437 mg L^{-1}), chloride (4.5 - 193 mg L^{-1}), sulfate (4.9 - 71 mg L^{-1}) and nitrate (1.7 - 9 mg L^{-1}).

The concentration of trace elements in TAR water shows patterns of behavior linked to source contribution and anthropogenic activities around the river and its tributaries. The large inter- and intra-site variations are partly due to real environmental changes. These variations could not be due to contamination, as we have followed the standard procedure for sampling and transport (22) and the same kind of care during both campaigns.

The direct solid and liquid waste discharge from different industrial, municipal and domestic activities at different locations exert a major influence on the trace

Table 5. Dissolved trace metal concentrations, $\mu\text{g L}^{-1}$, in the Tinishu Akaki River

Sampling site	Latitude/Longitude	Elevation (m)	Campaign	Concentrations (95 % C.I.)							
				Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
S1	N09°04.340' E038°38.064'	2611	I	-	-	-	-	-	-	-	-
			II	0.005 (0.001)	0.32 (0.003)	0.13 (0.01)	2.08 (0.07)	158 (1)	3.87 (0.05)	0.06 (0.013)	11.67 (0.06)
S2	N09°03.50' E038°40.806'	2507	I	0.003 (0.001)	0.45 (0.02)	0.32 (0.01)	1.07 (0.05)	236 (3)	1.35 (0.07)	0.055 (0.001)	7.67 (0.19)
			II	0.063 (0.001)	0.42 (0.01)	0.42 (0.01)	15.84 (0.04)	99.1 (0.4)	2.25 (0.03)	1.69 (0.01)	66.57 (0.68)
S3	N09°03.491' E038°40.798'	2511	I	0.009 (0.001)	0.23 (0.01)	0.32 (0.01)	1.1 (0.10)	85 (1)	1.09 (0.03)	0.059 (0.013)	7.75 (1.15)
			II	0.016 (0.001)	0.202 (0.004)	0.43 (0.01)	5.01 (0.04)	51.2 (0.5)	2.84 (0.04)	0.5 (0.03)	11.86 (0.1)
S4	N09°03.456' E038°40.821'	2511	I	0.005 (0.001)	0.25 (0.01)	0.36 (0.02)	1.13 (0.03)	88 (2)	1.09 (0.06)	0.041 (0.008)	3.02 (0.19)
			II	0.045 (0.003)	0.190 (0.004)	0.22 (0.01)	8.62 (0.07)	40.5 (0.1)	1.42 (0.03)	0.62 (0.01)	43.14 (0.36)
S5	N09°03.080' E038°41.188'	2467	I	0.006 (0.001)	0.35 (0.01)	0.34 (0.01)	1.22 (0.01)	131 (1)	1.0 (0.1)	0.057 (0.008)	2.43 (0.01)
			II	0.004 (0.001)	0.29 (0.004)	0.45 (0.02)	1.22 (0.05)	72 (0.3)	1.47 (0.03)	0.17 (0.01)	2.19 (0.05)
S6	N09°02942' E038°41.322'	2462	I	0.003 (0.001)	0.28 (0.01)	2.79 (0.02)	10.02 (0.11)	75 (1)	1.08 (0.03)	0.96 (0.03)	23.63 (0.31)
			II	0.03 (0.004)	1.374 (0.008)	14.42 (0.04)	8.6 (0.1)	283.6 (1.2)	3.88 (0.32)	1.22 (0.08)	27.87 (0.38)
S7	N09°02.931' E038°41.317'	2464	I	0.024 (0.001)	0.58 (0.01)	110.9 (0.7)	13.34 (0.42)	103 (1)	1.67 (0.04)	3.36 (0.06)	22.46 (0.79)
			II	0.032 (0.001)	0.43 (0.006)	264.2 (2.2)	1.24 (0.12)	28.2 (0.2)	1.62 (0.02)	0.09 (0.01)	5.23 (0.31)
S8	N09°02.829' E03841.329'	2455	I	0.022 (0.006)	0.52 (0.01)	104.3 (1.1)	4.07 (0.29)	138 (2)	2.18 (0.11)	0.31 (0.04)	12.96 (2.02)
			II	0.02 (0.004)	0.52 (0.01)	189.01 (1.22)	2.16 (0.04)	51 (0.4)	3.07 (0.07)	0.046 (0.01)	8.98 (0.15)
S9	N09°02.532' E038°41.615'	2428	I	0.056 (0.007)	0.74 (0.02)	50.43 (0.71)	2.81 (0.07)	444 (6)	2.14 (0.13)	0.304 (0.076)	8.49 (0.44)
			II	0.007 (0.002)	1.23 (0.02)	97.37 (0.83)	1.78 (0.1)	717 (10)	3.4 (0.1)	0.07 (0.01)	4.91 (0.28)
S10	N09°01.233' E038°42.017'	2368	I	0.012 (0.001)	1.9 (0.01)	9.63 (0.11)	1.83 (0.11)	1463 (65)	3.14 (0.06)	0.155 (0.022)	4.5 (0.15)
			II	0.019 (0.002)	1.16 (0.01)	0.09 (0.01)	0.55 (0.03)	1032 (6)	3.67 (0.08)	0.026 (0.007)	2.26 (0.06)

Table 5. (continued)

Sampling site	Latitude/Longitude	Elevation (m)	Campaign	Concentrations (95 % C.I.)							
				Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
S11	N09°01.220' E038°42.098'	2362	I	0.009 (0.001)	1.41 (0.01)	9.97 (0.08)	2.60 (0.11)	1114 (90)	3.08 (0.04)	0.11 (0.01)	10.95 (0.19)
			II	0.016 (0.002)	2.3 (0.03)	6.99 (0.03)	5.53 (0.1)	906 (5)	5.13 (0.08)	0.44 (0.02)	24.3 (0.9)
S12	N09°01.248' E038°42.539'	2367	I	0.01 (0.001)	1.94 (0.04)	0.95 (0.06)	17.09 (0.19)	1825 (24)	4.35 (0.19)	6.22 (0.31)	28.78 (1.03)
			II	0.004 (0.001)	4.93 (0.03)	1.02 (0.02)	0.84 (0.04)	2909 (10)	7.58 (0.09)	0.07 (0.01)	3.98 (0.21)
S13	N09°01.134' E038°42.575'	2343	I	0.02 (0.001)	1.63 (0.03)	7.65 (0.17)	2.5 (0.32)	955 (16)	4.42 (0.1)	0.09 (0.01)	2.11 (0.28)
			II	0.007 (0.001)	2.34 (0.01)	4.92 (0.03)	1.54 (0.04)	1071 (4)	5.37 (0.06)	0.023 (0.003)	1.74 (0.13)
S14	N09°00.430' E038°42.656'	2327	I	0.008 (0.001)	1.41 (0.01)	4.30 (0.06)	2.67 (0.07)	1224 (12)	3.49 (0.05)	0.258 (0.018)	3.24 (0.08)
			II	0.004 (0.001)	2.34 (0.04)	3.05 (0.07)	1.57 (0.19)	1198 (5)	5.83 (0.23)	0.054 (0.004)	2.25 (0.06)
S15	N08°59.259' E038°42.607'	2313	I	0.002 (0.001)	1.32 (0.04)	2.50 (0.08)	8.73 (0.31)	1236 (11)	4.71 (0.3)	1.73 (0.18)	16.69 (3.06)
			II	0.005 (0.001)	1.67 (0.02)	2.47 (0.04)	0.90 (0.05)	940 (9)	3.97 (0.03)	0.043 (0.006)	2.68 (0.16)
S16	N08°58.243' E038°43.578'	2221	I	-	-	-	-	-	-	-	-
			II	0.032 (0.004)	2.78 (0.01)	1.32 (0.01)	1.6 (0.17)	1297 (7)	5.36 (0.06)	0.55 (0.06)	8.74 (0.14)
S17	N08°58.338' E038°44.008'	2224	I	0.011 (0.001)	4.6 (0.04)	1.41 (0.06)	7.65 (0.21)	1101 (42)	7.89 (0.13)	2.66 (0.08)	13.4 (0.97)
			II	0.031 (0.003)	2.64 (0.04)	1.67 (0.06)	1.31 (0.04)	1590 (79)	5.27 (0.18)	0.35 (0.01)	6.09 (0.11)
S18	N08°57.658' E038°44.623'	2194	I	0.007 (0.001)	2.85 (0.04)	1.72 (0.07)	1.11 (0.11)	1727 (17)	5.87 (0.1)	0.144 (0.018)	2.57 (0.08)
			II	0.011 (0.001)	2.72 (0.04)	1.29 (0.06)	1.61 (0.06)	1510 (31)	7.6 (0.2)	0.141 (0.01)	5.76 (0.5)
S19	N08°57.448' E038°44.961'	2215	I	0.037 (0.004)	2.32 (0.03)	2.06 (0.11)	1.09 (0.04)	1586 (9)	4.36 (0.13)	0.15 (0.01)	2.34 (0.17)
			II	0.023 (0.003)	2.36 (0.01)	2.06 (0.03)	5.89 (0.06)	1460 (25)	5.05 (0.06)	1.11 (0.01)	18.49 (0.3)
S20	N08°56.978' E038°45.562'	2201	I	1.17 (0.065)	3.63 (0.06)	1.48 (0.07)	27.76 (0.14)	1220 (5)	19.48 (0.18)	4.92 (0.39)	593.82 (1.81)
			II	0.057 (0.004)	2.98 (0.01)	1.88 (0.03)	11.2 (0.93)	1610 (19)	6.37 (0.03)	1.77 (0.11)	27.59 (1)

Table 5. (continued)

Sampling site	Latitude/ Longitude	Elevation (m)	Campaign	Concentrations (95 % C.I.)							
				Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
S21	N08°56.826' E038°45.562'	2194	I	0.021 (0.001)	3.71 (0.05)	2.69 (0.04)	2.63 (0.15)	1737 (18)	8.81 (0.22)	3.28 (0.19)	8.56 (0.31)
			II	0.034 (0.006)	3.04 (0.04)	2.43 (0.03)	6.47 (0.11)	1567 (39)	5.59 (0.07)	1.34 (0.08)	18.44 (0.36)
S22	N08°55.867' E038°45.428'	2174	I	0.017 (0.004)	3.38 (0.02)	11.26 (0.07)	1.69 (0.07)	1911 (40)	7.54 (0.1)	0.235 (0.024)	2.74 (0.44)
			II	0.074 (0.004)	3.77 (0.04)	54.22 (0.21)	20.76 (0.08)	1897 (21)	7.53 (0.04)	4.73 (0.13)	70.1 (0.5)
S23	N08°51.873' E038°44.394'	2069	I	0.018 (0.003)	4.05 (0.03)	3.07 (0.08)	3.26 (0.04)	1250 (38)	9.07 (0.11)	0.159 (0.014)	6.11 (0.23)
			II	0.051 (0.004)	2.63 (0.08)	8.51 (0.14)	14.9 (1.1)	1397 (14)	7.6 (0.3)	1.3 (0.06)	35.42 (0.92)
Mean for all sampling points			I	0.070	1.788	15.64	5.49	854.2	4.66	1.202	37.34
			II	0.026	1.850	28.63	5.27	951.5	4.60	0.713	17.84
Surface water quality standard class 2 - 4				5*							
				50**	-	50	100	1000	100	50	1000
Irrigation water				10	50	100	200	200	200	5000	2000

* When water hardness not more than 100 mg L⁻¹ as CaCO₃; ** When water hardness more than 100 mg L⁻¹ as CaCO₃

element chemistry of TAR.

The different tributaries also contribute to the trace element concentration. Most of them receive all kinds of wastes and then finally join the TAR. Some of the tributaries are relatively clean and play a dilution role.

Finally, the chemical erosion of the earth's crust, the urban and surface runoff due to high intensity rain fall prior to the second sampling campaign and the diversion of TAR water for irrigation purposes at different sites along the river contribute to the inter- and intra-site variations.

It was hypothesized that contamination (with heavy metals) would be more marked in the downstream sites of the river. However, this hypothesis may be doubtful, as the water is diverted for irrigation purposes at different points along the river. Moreover, the low concentration is in agreement with the pH values found for those waters (7.2-8.8). Owing to their low concentrations, precipitation as carbonate or hydroxide is not very probable. Adsorption to humic acid and colloidal iron oxides (28) may be a better explanation.

The elemental concentrations of Cd, Co, Cu, Ni, Pb

and Zn measured in water samples from the TAR fulfill the surface water quality standard (29) of class 2- class 4 (Table 5). Thus, there is an indication that it may be used as irrigation water (30). Cr at site number S7-S9, during both campaigns, and S22, during campaign II, does not fulfill class 2 – 4 water quality criteria (29). Consequently, water samples from S7 and S8 were, during both campaigns, not appropriate for use as irrigation water (30).

In the case of Mn, water samples from S10, S12, S14-S23 (campaign I); S10, S12-S14 and S16-S23 (campaign II) do not fulfill the surface water quality criteria of class 2 - 4, and water samples from S2, S9, S10, S12-S23, campaign I; S6, S9-S23, campaign II, showed that water from these sites is unfit for irrigation purposes.

The probable sources of trace elements in TAR water vary widely and may include wastewaters generated municipally, domestically and industrially and/or wastes from intensive agricultural practices, the major occupation of the people in the study area.

Chromium enters TAR water as a result of direct

effluent discharge from Addis Ababa and Batu tanneries, located upstream from sampling site S6 and S22, respectively. Manganese could result from the chemical erosion of the earth's crust, but more probably it is from some industrial activity, such as distilleries, a battery factory and public and domestic waste, especially from hospitals where permanganate is used as an oxidizing agent. In spite of the above, TAR water is used to grow vegetables, water animals, etc.

Conclusions

ICP-MS data were validated for several elements (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) by analysis of certified reference materials of wastewater and riverine water origins. The described procedure was used for the determination of trace elements in Tinishu Akaki river water samples. This work has shown that, although analyses with external calibrations are usually more subject to errors arising from ionization interferences (caused by concomitant elements) in ICP-MS, the use of Sc, In and Tl as internal standards in addition to appropriate dilution of water sample proved mostly to be efficient to correct for ICP-MS drift and matrix effects.

The merits of ICP-MS as a technique for the simultaneous determination of trace elements in polluted river water have been demonstrated. ICP-MS is an excellent analytical technique for surveying heavy metals in water.

It has been evident from our findings that the causes and sources of water pollution in the study area are mainly anthropogenic activities through the direct discharge of effluents from different industries.

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References

1. M. Miro, J.M. Estela and V. Cerda, *Talanta*, **63**, 201 (2004).
2. S.K. Lee and H.S. Choi, *Bull. Korean Chem. Soc.*, **22**, 463 (2001).
3. S.J. Hill, T.A. Arowolo, O.T. Butler, J.M. Cook,

- M.S. Cresser, C. Harrington and D.L. Miles, *J. Anal. At. Spectrom.*, **19**, 301 (2004).
4. S. Kagaya, Y. Hosomori, H. Arai and K. Hagegawa, *Anal. Sci.*, **19**, 1061 (2003).
5. I.O.B. Ewa, S. Ebele and I.M. Umar, *J. Trace and Microprobe Techn.*, **20**, 385 (2002).
6. M. Dogan and M. Soylak, *J. Trace and Microprobe Techn.*, **20**, 261 (2002).
7. A.T. Townsend, J. O'Sullivan, A.M. Featherstone, E.C.V. Butler and D.J. Mackey, *J. Environ. Monit.*, **3**, 113 (2001).
8. H. Louie, M. Wu, P. Di, P. Snitch and G. Chapple, *J. Anal. At. Spectrom.*, **17**, 587 (2002).
9. Y.L. Chen and S.J. Jiang, *J. Anal. At. Spectrom.*, **15**, 1578 (2000).
10. C.Y. Ho and S.J. Jiang, *J. Anal. At. Spectrom.*, **17**, 688 (2002).
11. J.L. Fernandez-Turiel, J.F. Llorens, F. Lopez-Vera, C. Gomez-Artola, I. Morell and D. Gimeno, *Fresenius J. Anal. Chem.*, **386**, 601 (2000).
12. I.B. Brenner and H.E. Taylor, *Critical Rev. Anal. Chem.*, 355 (1992).
13. C. Reimann, U. Siwers, H. Scarphagen and D. Banks, *Sci. Total Environ.*, **234**, 155 (1999).
14. F. Vanhaecke, *Anal. Bioanal. Chem.*, **372**, 20 (2002).
15. J.T. Creed, C.A. Brockhoff and T.D. Martine, EPA/600/R-94/111 (1994).
16. K.H. Lee, M. Oshima, T. Takayanagi and S. Motomizu, *Anal. Sci.*, **16**, 731 (2000).
17. T.J. Hwang and S.J. Jiang, *Analyst*, **122**, 233 (1997).
18. <http://www.metropolis.org/metropolis/gcities.nsfHeadingPagesDisplayAfricaAddis+Ababa>About+Addis+Ababa?OpenDocument>
19. H. Selassie Girmay and G. Assefa, *The Addis Ababa-Nazaret Volcanics: A Miocene-Pleistocene volcanic succession in the Ethiopian Rift*. SINET: *Ethiop. J. Sci.*, **12**, 1 (1989).
20. http://www.waltainfo.com/Regional_States/AddisAbaba/A.A_Today.htm
21. A.A. Olajire and F.E. Imeokparia, *Environ. Monit. Assess.*, **69**, 17 (2001).
22. J. Bartram and R. Balance, *Water Quality Monitoring: A practical guide to the design and implementation of fresh water quality studies and monitoring programmes*. First

- edition. Chapman & Hall, London, 1996, p. 71.
23. L.S. Clesceri, A.E. Greenberg, A.D. Eaton and M.A.H. Franson, *Standard Methods For The Examination of Water and Wastewater*, 20th Edition, United Book Press, Maryland, 1998.
 24. C. Gueguen, R. Gilbin, M. Pardos and J. Dominik, *App. Geochem.*, **19**, 153 (2004).
 25. L. Moens, H. Vanhoe, F. Vanhaecke, J. Goossens, M. Campbell and R. Dams, *J. Anal. At. Spectrom.*, **9**, 187 (1994).
 26. L. Moens and R. Dams, *J. Radioanal. Chem.*, **192**, 29 (1995).
 27. P. Abbyad, J. Tromp, J. Lam and E. Salin, *J. Anal. At. Spectrom.*, **16**, 464 (2001).
 28. J.M. Bubb and J.N. Lester, *Sci. Total Environ.*, **100**, 207 (1991).
 29. <http://www.pcd.go.th/information/regulations/waterquality/SurfaceWater.htm#Class>
 30. M. Csuros and C. Crusos, *Environmental Sampling and Analysis for Metals*, CRC press LLC, Florida, USA, 2002, p. 72.