

# Optimization of Major and Trace Elements Determination in Acid Mine Drainage Water Samples by USN-ICP-OES

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## 1. Definition

### Acid Mine Drainage (AMD)

Environmental oxidation of sulphides enrich residues from mine activities e.g. tailings, waste rock, mining and waste material Fe, Mn, Cu, Pb, Zn, Cd, As

### Acid Rock Drainage (ARD)

In ARD the matrix can be complex with high concentrations of S, Fe, Mn, Al, Cu. ICP-MS is OK for traces (with dilution), but larger dilutions are required for majors, leading to much sample preparation and possible errors due to large dilution factors.

USN-ICP-OES allows for the determination of all elements in a single analysis run

## 2. Introduction

Analysis can be from ppb to % levels, with the matrices quite variable leading to difficulties to matrix match and no suitable standards or CRM's are available. There is also high dissolved solids and the technique of standard addition might cause trace element interferences. This work will show that an in house standard choosing a Tinto river sample with similar matrix was suitable for spiked additions.

## 3. Sample preparation

Samples were collected from the Tinto and Odiel rivers (an estuary near Huelva), the 0.45µm filtered samples were stored at 4°C and stabilised in 0.2% HNO<sub>3</sub>. Some composite Tinto river samples were stored short term at 4°C in a fridge, while long term storage was done with samples frozen in a freezer.

## 4. Instrumentation

The work was done on a JY ULTIMA 2. The specifications of this instrument are listed below in Tables 1 and 2.

Table 1: Specification of spectrometer

Parameters	Specifications
Mounting	Czerny Turner
Focal length	1m
Nitrogen purge	Yes
Resolution	5 pm
Grating number of grooves	2400 gr/mm
Order	2nd order

Table 2: Specification of RF Generator

Parameters	Specifications
Type of generator	Solid state
Observation	Radial
Frequency	40.68 MHz
Control of gas flowrate	by computer
Control of pump flow	by computer
Cooling	air

The operating conditions are listed in Table 3 below.

Table 3: Operating conditions

Parameter	Condition
RF Generator power	1200 W
Plasma gas flowrate	15 L/min
Auxiliary gas flowrate	0.2 L/min
Sheath gas flowrate	0.6 L/min
Sample uptake	1 mL/min
Type of nebulizer	USN Cetac U-6000 AI with dissolution system
Injector tube diameter	3.0 mm

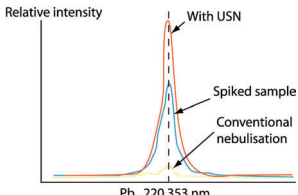


Figure 1: Effect of USN with ICP-OES

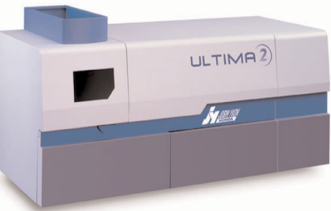


Figure 2: ULTIMA 2

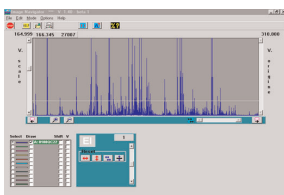
## 4. Identification of wavelengths to use via Win Image

Win Image gives the full spectrum analysis of > 450,000 data points with a 0.5 ms dwell time.

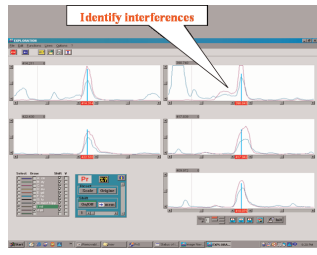
The lines are chosen from the following criteria:

- Clean line – no interferences
- Capability of determining the low and the high concs required
- Recoveries generally 70-95%
- Linear response to the concentration range required

CRM's used to validate method and lines chosen.



Complete spectrum acquisition in less than 2-3 mins (depends on parameters) without any user calibration



High resolution enables Cd 228.8 to be used

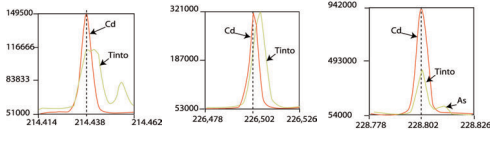


Figure 5: Cd lines in river Tinto

## 6. Results

### 6.1 Typical concentration range in Tinto river Sample

Table 4

Element	Range	Element	Range
S	100 - 3000 ppm	K	0 - 5 ppm
Fe	2 - 4000	Li	0 - 2
Mg	10 - 1000	Ba	0 - 1
Ca	0 - 500	Be	0 - 0.1
Al	0 - 300	Cd	0 - 1
Zn	4 - 250	Co	0 - 5
Cu	2 - 50	Cr	0 - 0.1
Mn	2 - 30	Ni	0 - 2
Si	0.1 - 30	P	0 - 1
As	0 - 20	Pb	0 - 1
Na	0 - 60	Sb	0 - 0.05
TI	0 - 0.3	Se	0.01 - 0.05
V	0 - 0.1	Sn	0 - 0.05

### 6.1 Limits of detection

Table 5

Wavelength	LOD	Wavelength	LOD
Al	286.039 3.11 µg/l	Mn	259.373 248 ng/l
As	189.042 207 ng/l	Mo	204.598 70 ng/l
Ba	455.403 15 ng/l	Na	589.592 285 ng/l
Be	313.042 5.9 ng/l	Ni	221.647 1.6 µg/l
Bi	422.673 33.9 ng/l	P	213.618 1.7 µg/l
Cd	228.802 37 ng/l	Pb	220.353 78 ng/l
Co	228.616 272 ng/l	S	181.978 42 µg/l
Cr	267.716 13 ng/l	Sb	217.581 333 ng/l
Cu	213.598 217 ng/l	Se	196.026 319 ng/l
Fe	282.167 125 µg/l	Si	212.412 3.5 µg/l
K	766.490 1.6 µg/l	Sn	189.930 21 ng/l
Li	670.784 258 ng/l	Sr	407.771 4.1 ng/l
Mg	382.935 10 ng/l	TI	351.924 1.6 µg/l
		V	311.868 12 ng/l
		Zn	334.502 13 µg/l

Many wavelengths are primary lines, (blue) due to the resolution of the spectrometer (5pm). Some lines chosen for their high concentration range (red)

### 6.2 Accuracy validation

Table 6: Various spikes on Tinto sample 1:2 dilution (10 replicates). Results are in mg/L

Tinto Spiked	Theo Conc	% Recovery	Tinto	Theo Conc	% Recovery
Al	155	86	155	215	72
As	2.01	2.26	89	2.40	3.11
Ba	0.015	0.027	55	0.022	0.046
Be	0.017	0.018	96	0.024	0.027
K	106	127	84	125	168
Cd	0.40	0.50	80	0.461	0.664
Co	1.66	1.94	86	2.102	2.830
Cr	0.08	0.10	78	0.101	0.144
Cu	46.61	54.2	86	2.1	70.25
Fe	1071	1121	95	1248	1438
K	6.21	5.16	120	8.2	6.8
Li	0.60	0.55	109	0.66	0.69
Mg	178	195	91	177	228
Mn	15.9	17.8	89	16.0	21.3
Mo	0.08	0.11	77	0.14	0.20
Na	77.9	65.9	118	101	81
Ni	0.42	0.5	85	0.46	0.66
P	0.34	0.5	69	0.39	0.55
Pb	0.24	0.28	88	0.28	0.36
K	6.21	5.16	120	8.2	6.8
Li	0.60	0.55	109	0.66	0.69
Mg	178	195	91	177	228
Mn	15.9	17.8	89	16.0	21.3
Mo	0.08	0.11	77	0.14	0.20
Na	77.9	65.9	118	101	81
Ni	0.42	0.5	85	0.46	0.66
P	0.34	0.5	69	0.39	0.55
Pb	0.24	0.28	88	0.28	0.36

- Negative bias of results
- Recoveries generally 70-95%
- Alkalis elements (Na, Li, K) exhibit 111-125% enhancement. Probably due to ionisation

### 6.4 Matrix interference studies (mg/l)

Table 7

Tinto	Tinto	Tinto	Rel error	Rel error	
No spike	1:10 dil	1:20 dil	1:20	1:10	
Al	152	194	196	22	23
As	1.5	2.0	1.9	25	24
Ba	0.008	0.005	0.009	- 61	7
Be	0.009	0.03	0.02	69	53
Ca	90	112	108	20	17
Cd	0.348	0.46	0.45	25	22
Co	1.09	1.51	1.50	28	27
Cr	0.06	0.14	0.11	59	46
Cu	40	47	46	15	14
Fe	839	805	817	- 4	- 3
K	3.7	2.7	3.0	- 36	- 21
Li	0.53	0.45	0.45	- 18	- 16
Mg	169	182	184	7	8
Mn	15	22	21	31	28
Mo	0.006	0.03	0.02	82	74
Na	53	35	35	- 54	- 49
Ni	0.35	0.65	0.56	46	38
P	0.46	0.58	0.45	20	- 4
Pb	0.21	0.34	0.31	40	33
S	1249	1591	1525	21	18
Sb	n.d.	n.d.	n.d.	-	-
Se	0.012	0.011	0.016	- 17	22
Si	26	26	26	1	0
Sn	0.012	0.21	0.09	94	87
Sr	0.20	0.27	0.26	25	21
TI	n.d.	n.d.	n.d.	-	-
V	0.009	0.041	0.024	79	64
Zn	91	122	122	25	25

- Tinto River water results show a matrix interference. Generally a 20% negative bias neat (without dilution) compared with x 10 and x 20 dilution

- Ba, Mo and V disagreement may be due to proximity with LOD

- Alkalis elements (Na, Li and K) exhibit a ~30% enhancement probably due to ionisation.

### 6.5 Spiked recoveries

Table 8: on diluted Tinto river 1:20 dilution

Tinto	C spiked	% recovery	C spiked	% recovery
1:20 dil	50 %		100 %	
Al	9.94	14.85	99	20.48
As	0.10	0.15	97	0.21
Ba	Not spiked	Not spiked	Not spiked	Not spiked
Be	Not spiked	Not spiked	Not spiked	Not spiked
Ca	5.76	8.80	106	11.69
Cd	0.02	0.03	93	0.05
Co	0.08	0.11	94	0.17
Cr	0.01	0.01	98	0.01
Cu	2.39	3.67	107	5.11
Fe	41.3	62.8	104	81.51
K	0.14	0.21	96	0.28
Li	0.02	0.03	105	0.05
Mg	9.34	14.06	101	19.53
Mo	0.03	0.05	104	0.07
Ni	Not spiked	Not spiked	Not spiked	Not spiked
Na	1.78	2.71	105	3.56
Ni	0.03	0.05	94	0.07
P	0.03	0.04	94	0.06
Pb	0.02	0.03	96	0.04
S	81.7	122	100	172
Sb	Not spiked	Not spiked	Not spiked	Not spiked
Se	Not spiked	Not spiked	Not spiked	Not spiked
Si	1.34	1.98	94	2.65
Sn	0.01	0.02	100	0.02
Sr	0.01	0.02	100	0.03
TI	Not spiked	Not spiked	Not spiked	Not spiked
V	Not spiked	Not spiked	Not spiked	Not spiked
Zn	6.27	9.27	96	12.66

Table 9: on diluted Tinto river 1:10 dilution

Tinto	C spiked	% recovery	C spiked	% recovery
1:10 dil	50 %		100 %	
Al	19.9	29.0	92	43.49
As	0.19	0.31	117	0.40
Ba	No spike	NS	No spike	No spike
Be	No spike	NS	No spike	No spike
Ca	11.00	16.96	108	23.6
Cd	0.05	0.07	100	0.09
Co	0.15	0.24	113	0.30
Cr	0.01	0.02	104	0.02
Cu	4.68	6.939	61	0.05
Fe	83	127	106	172
K	0.31	0.46	96	0.63
Li	0.05	0.07	115	0.09
Mg	18.7	29.5	116	39.5
Mn	2.1	3.3	111	4.48
Mo	NS	NS	NS	Not spiked
Na	3.65	5.39	96	7.47
Ni	0.06	0.09	111	0.12
P	0.05	0.07	117	0.09
Pb	0.03	0.05	104	0.06
S	155	241	111	317
Sb	NS	NS	NS	Not spiked
Se	NS	NS	NS	Not spiked
Si	2.63	4.09	111	5.64
Sn	0.01	0.01	96	0.02
Sr	0.03	0.04	111	0.05
TI	NS	NS	NS	Not spiked
V	NS	NS	NS	Not spiked
Zn	12.39	18.78	103	25.39