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Determination of total elements in the topsoil rice field Ambohitrimanjaka using Energy Dispersive X-ray Fluorescence

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***Abstract**: This work was carried out at the laboratory INSTN-Madagascar. The aim of this study is to determine the total elements in term of major, minor and traces elements in the topsoil rice land culture. The samples were taken at the village of Ambodivona in the township of Ambohitrimanjaka. Energy Dispersive X-ray Fluorescence (EDXRF) technique was used for the elemental analysis of soil samples.*

The results showed that all soils are very acidic. The range of pH of soils in water was from 4.3 to 5.34. In general, the value of pH for soils in agriculture is between 4.30 and 5.19 which is equivalent to one slightly acidic soil. In addition, the range of pH adapted for soils in rice culture is from 6 to 7. All soil samples contain the elements such as potassium (K), calcium (Ca),titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), cooper (Cu), zinc (Zn), gallium (Ga), bromine (Br), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), gadolimium (Gd), terbium (Tb), and lead (Pb are in trace).The major elements are composed by K, Ca, Fe and Sr but the others elements like M, Cu, Zn,Br, Rb and Pb are minor. The analysed soil samples are very rich in potassium. But, they had a deficiency made of calcium and the excesses of Mn and Co could be due to the acidic nature of soils. The deficiency made of calcium and the excesses of Mn, Co and Br could be one factor of the illness of the plants and involve to the low yield productivity.

***Keywords**: X-ray Fluorescence, major, minor and traces elements, soil*

I. Introduction

Rice is the principal food of the Malagasy people. In fact, the basic knowledge of the quality of the soil in rice field was one of the parameters for increasing rice products. In term of total elements, X-ray fluorescence (XRF) technique was used for the determination of heavy metals in soil such as arsenic (As), cooper (Cu), vanadium (V), chromium (Cr), nickel (Ni), lead (Pb) and zinc (Zn) (ANTOANETA ENE, 2010). The investigation of soil analysis by using XRF technique in Kumasi, Ghana showed that this technique was used to determine the concentration of the nine heavy metals like zinc (Zn), lead (Pb), chromium (Cr), cooper (Cu), cobalt (Co), nickel (Ni), cadmium (Cd), mercury (Hg) and arsenic (As) (K. KODOM et al, 2012). Total reflection X-Ray Fluorescence (TXRF) also was developed and was proved a method for direct quantification of elements in soil and it is suitable for the determination of the concentration of major and trace elements in multiple media (Erick K. Towett, 2013). The obtained results showed that the application of XRF method gives the possibility to realize quick multielement soil analysis and speciation analysis (R. Baranowski, 2002). For using XRF technique, the analyst must take into account the optimal experimental parameters for XRF spectrometer analysis of soil such as the thickness of soil sample, the grain size of particles of soil sample and the water content in soils sample (Yukiko Imanishi, 2010).
The aim of this study is to assess the total elements concentration in the topsoil from the rice land field using energy dispersive X-ray fluorescence.

II. Materials and methods

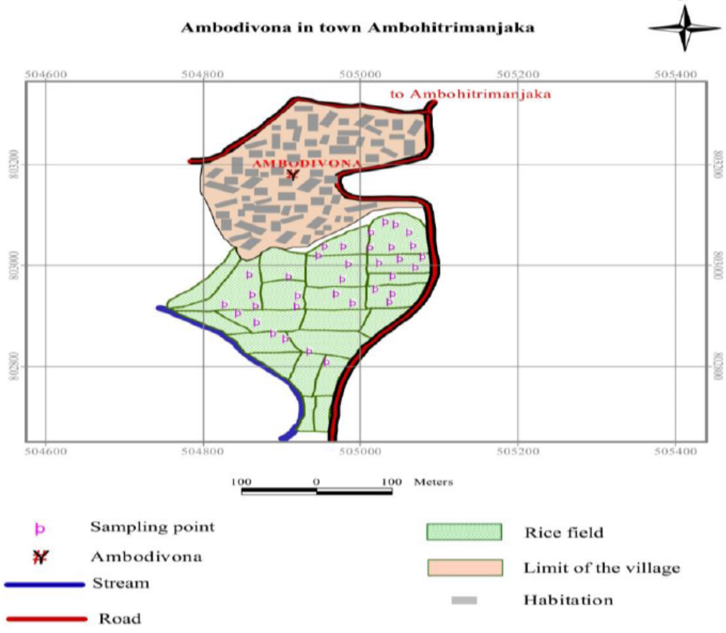
X-ray spectrometer was used to determine the total elements in the topsoil. It was composed by X-ray tube with molybdenum (Mo) anode, pre amplifier, amplifier, multichannel analyzer and a computer which contain both AXIL and QXAS (Quantitative X-ray Analysis System) programs and a Si(Li) detector. The distance between incident beam-sample and sample-detector were 3 cm and 6 cm respectively. Molybdenum (Mo) and iron (Fe) were used as secondary target.

III. Sampling and Sample preparation

III.1 Sampling

Soil samples were taken at rice field located at Ambodivona in the township of Ambohitrimanjaka. The distance between each sampling site varied from 50 m to 70 m and soil samples were taken in deep from 15 cm to 20 cm. Codified plastic bags was used as sample carrier. 35 samples were collected from the study area. Each sampling point was recorded with GPS (Geographic Position System) . Then, all sampling sites were situated between 18° 52′ 09,2″ and 18° 52′ 18,7″ S and 47° 25′ 59,8″ and 47° 26′ 08,8″ E. Figure 1 shows the spatial distribution of each sampling point.

Figure 1: Spatial distribution of each sampling point



III.2 Sample preparation

The objective of the sample preparation is to transform soil samples into pellets. Soil samples were dried in a furnace at temperature 500°C during 30 minutes to remove the organic matrix effects (IAEA-Tecdoc-300, 1983). Then, each sample was pulverized until the grain size was less than 50 µm (IAEA-Tecdoc-950, 1997). After, homogenized samples were dried in an electric oven during 24 hours at 105°C for dehumidification (IAEA Soil-7 Certified Reference Materials, 1984). Finally, soil samples were transformed into thick pellet under pressure 10 tons using manual hydraulic press SPECAC. Three pellets per sampling point were prepared.

IV. Experimental conditions and analysis

Experimental conditions:

The following parameters were used during the experiment:

For secondary target Molydenum (Mo)

- Tube power : 40 kV
- Tube current : 15 mA
- Counting time : 1000 s

For secondary target iron (Fe)

- Tube power : 35 kV
- Tube current : 15 mA
- Counting time : 1000 s

All samples were measured in three times at the two conditions cited above.

Analysis

It is based on the qualitative and quantitative determination of the elements in the analyzed samples. Both, AXIL and Q.X.A.S. programs were used for spectrum deconvolution and quantitative analysis respectively. “ELEMENTAL SENSITIVITIES” method was used for quantitative analysis. Merck products were used to calibrate the X-ray spectrometer. Then, the results of the calibration curves are reported on the figures 2, 3 and 4.

Figure 2. Variation of the elemental sensitivity versus atomic number for K-lines with secondary target Mo

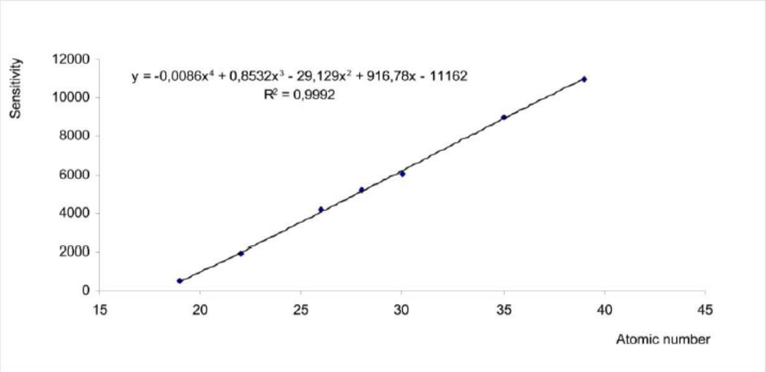


Figure 3. Variation of the elemental sensitivity versus atomic number for L-lines with secondary target Mo

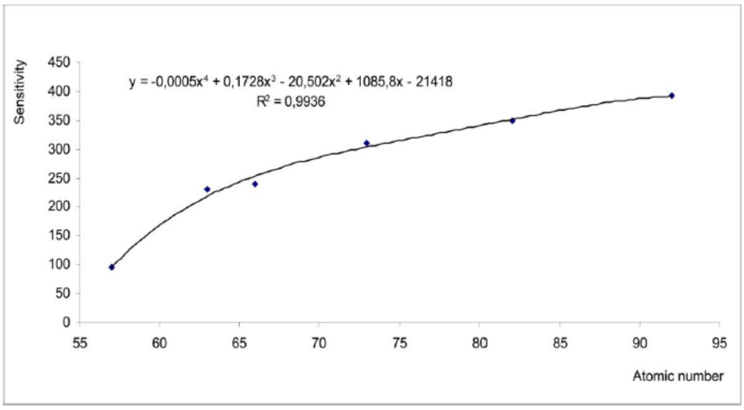
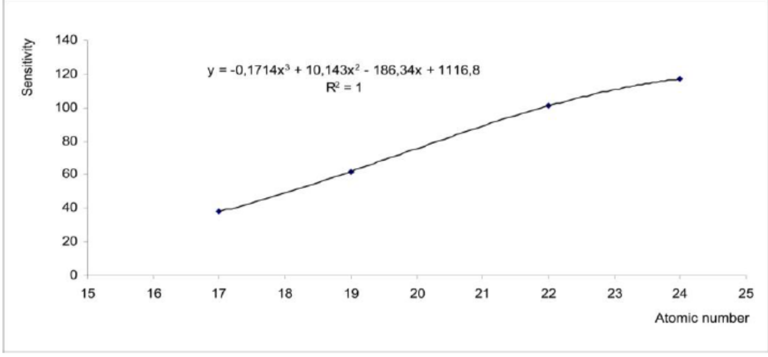


Figure 4. Variation of the elemental sensitivity versus atomic number for K-lines with secondary target Fe



Detection limit

The following formula was used to calculate the detection limit related on the concentration. It was expressed in mg/kg.

$$\left(C_{LD}\right)_i = 3\,C_i \frac{1}{N_i}\sqrt{\frac{t}{1000}}\sqrt{(N_B)_i}$$

where

C_i: Concentration of the element i

$(N_B)_i$: Background of the element i

(N_i): Net area of the element i

IAEA Certified Reference Materials soil-7 was used to determine the detection limit. Tables 1, 2 and 3 show the obtained results for secondary target Fe and Mo respectively.

Table 1. Detection limit for K-lines using secondary target Fe

Elements	Atomic number (Z)	Detection limit in mg/kg
K	19	319
Ca	20	249
Ti	22	42
V	23	13
Cr	24	32
Mn	25	50

Table 2. Detection limit for K-lines using secondary target Mo

Elements	Atomic number (Z)	Detection limit in mg/kg
Fe	26	112
Co	27	78
Cu	29	11
Zn	30	10
Ga	31	9
Br	35	6
Rb	37	5
Sr	38	5
Y	39	3
Zr	40	50

Table 3. Detection limit for L-lines using secondary target Mo

Elements	Atomic number (Z)	Detection limit in mg/kg
Gd	64	145
Tb	65	137
Pb	82	10

Method quality control

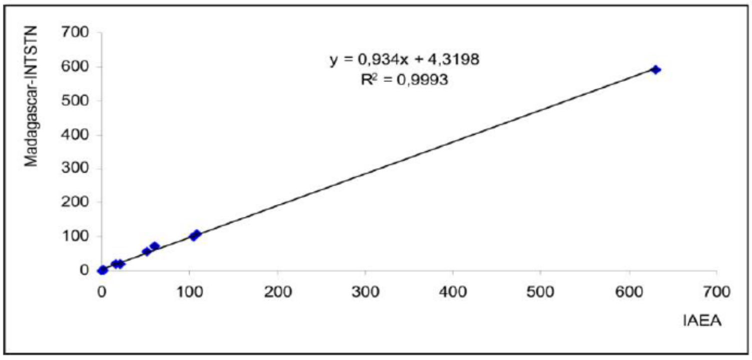
To evaluate the accuracy and the efficiency of the method to be used, IAEA Reference Certified Materials soil-7 was analyzed with respect of the sample preparation recommended in the paper (IAEA Soil 7 Certified Reference Materials, 1984). Table 4 gives both the experimental values determined by INSTN-Madagascar- and the certified values given by IAEA.

Table 4. Comparison of Soil-7 results between experimental values by Madagascar-INSTN and IAEA certified values

Elements	Unit	IAEA Certified values	Determined values by INSTN-Madagascar	Absolute difference
Potassium (K)	%	1.21 ± 0.01	1.84 ± 0.07	0.63
Calcium (Ca)	%	16.3 ± 0.25	19.6 ± 0.64	3.3
Titane (Ti)	%	0.3 ± 0.02	0.3 ± 0.02	0
Manganèse (Mn)	mg/kg	631 ± 4.00	592 ± 43.00	39
Fer (Fe)	%	2.57 ± 0.01	2.77 ± 0.13	0.2
Zinc (Zn)	mg/kg	104 ± 3.00	102 ± 4.03	2
Rubidium (Rb)	mg/kg	51 ± 0.50	55 ± 0.95	4
Strontium (Sr)	mg/kg	108 ± 0.50	108 ± 2.15	0
Yttrium (Y)	mg/kg	21 ± 0.00	20 ± 0.30	1
Plomb (Pb)	mg/kg	60 ± 3.00	71 ± 11.53	11

The results showed that experimental values are in good agreement with the certified values with regression coefficient in order of 0.9993. Figure 5 indicates the plotted of the two values.

Figure 5. Comparison between experimental values and IAEA certified values



IV. Results and discussion

In tables 5, 6, 7 and 8 which give the average concentration of the constituent elements of the analyzed soil samples, the K, Ca, Ti, V, Cr and Mn elements were quantified by using iron secondary target. As for the elements from Fe to Pb, the soil samples were irradiated by molybdenum secondary target.

Table 5. Average concentration of the elements in the analyzed soil samples (sample n°1 to sample n°7)

Elements	Unit	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
K	‰	3.51	2.45	2.85	3.17	1.80	2.62	3.75
Ca	‰	1.37	1.28	1.30	1.19	1.02	1.23	1.22
Ti	mg/kg	5 313.72	4 484.89	4 510.52	4 500.56	5 242.65	6 046.58	6 338.13
V	mg/kg	117.55	111.91	125.46	126.13	113.42	123.71	115.56
Cr	mg/kg	79.68	97.24	53.51	81.86	121.51	60.93	52.93
Mn	mg/kg	231.30	218.12	178.83	226.37	250.30	223.00	235.42
Fe	%	2.28	2.33	2.35	2.48	2.27	2.36	2.30
Co	mg/kg	161.33	< 78	< 78	188.34	< 78	131.83	< 78
Cu	mg/kg	51.42	54.27	51.39	51.21	66.79	48.40	60.36
Zn	mg/kg	107.17	107.08	99.41	105.04	92.60	92.72	113.56
Ga	mg/kg	29.01	32.77	35.27	24.91	31.62	42.77	31.57
Br	mg/kg	75.53	70.44	54.24	54.76	54.91	53.03	65.01
Rb	mg/kg	13.38	11.18	12.45	15.72	11.08	12.39	20.69
Sr	mg/kg	79.98	50.26	58.03	64.51	59.85	79.77	100.03
Y	mg/kg	25.85	28.94	35.47	26.29	27.18	34.46	34.89
Zr	mg/kg	341.92	288.04	309.85	393.80	328.23	402.90	469.91
Gd	mg/kg	309.08	< 145	< 145	490.66	< 145	447.93	< 145
Tb	mg/kg	1 337.11	1 767.46	1 353.32	1 601.47	1 555.94	1 838.99	1 684.46
Pb	mg/kg	29.43	23.89	35.71	30.29	30.27	28.03	32.28

Table 6. Average concentration of the elements in the analyzed soil samples (sample n°8 to sample n°14)

Elements	Unit	Sample 8	Sample 9	Sample 10	Sample 11	Sample 12	Sample 13	Sample 14
K	‰	2.96	3.60	4.78	4.06	7.79	3.92	3.32
Ca	‰	1.13	1.27	1.33	0.93	1.77	1.19	0.88
Ti	mg/kg	5 784.26	6 030.65	5 667.80	6 347.59	4 763.16	5 942.61	5 823.97
V	mg/kg	107.99	191.53	80.93	100.15	< 13	< 13	140.94
Cr	mg/kg	< 32	48.22	42.50	80.48	90.57	82.78	< 32
Mn	mg/kg	201.80	272.06	235.02	211.77	248.70	283.04	210.55
Fe	%	1.82	1.86	1.84	2.65	2.15	2.45	2.54
Co	mg/kg	< 78	< 78	< 78	132.24	< 78	< 78	< 78
Cu	mg/kg	< 11	< 11	< 11	45.29	53.55	61.71	51.62
Zn	mg/kg	99.25	83.73	93.76	120.63	103.55	124.79	114.35
Ga	mg/kg	37.45	32.85	36.10	41.14	25.20	34.34	36.22
Br	mg/kg	44.94	49.37	70.17	51.75	26.83	45.70	47.74
Rb	mg/kg	14.64	15.33	21.61	19.84	29.52	20.22	18.18
Sr	mg/kg	87.63	88.74	114.80	120.66	143.87	111.29	107.79
Y	mg/kg	33.13	28.83	29.74	33.34	30.84	33.33	36.70
Zr	mg/kg	380.01	352.16	351.68	554.49	720.21	518.50	422.80
Gd	mg/kg	4 094.87	4 119.19	3 929.34	< 145	< 145	< 145	< 145
Tb	mg/kg	2 776.99	2 799.04	2 801.24	1 611.74	1 270.22	1 489.51	1 646.15
Pb	mg/kg	30.55	27.97	27.06	33.77	30.97	38.54	33.08

Table 7. Average concentration of the elements in the analyzed soil samples (sample n°15 to sample n°21)

Elements	Unit	Sample 15	Sample 16	Sample 17	Sample 18	Sample 19	Sample 20	Sample 21
K	‰	2.90	2.79	3.59	3.48	2.62	5.26	4.57
Ca	‰	1.21	1.02	0.99	1.08	1.11	1.37	1.22
Ti	mg/kg	6 256.08	5 925.22	6 365.86	6 261.85	6 315.12	5 892.70	5 747.26
V	mg/kg	220.05	100.12	99.90	192.70	163.58	87.44	94.11
Cr	mg/kg	105.74	142.03	93.10	99.72	69.20	83.01	39.01
Mn	mg/kg	252.69	244.74	< 50	275.38	179.70	239.01	322.16
Fe	%	2.75	2.55	2.77	2.56	2.75	2.44	2.28
Co	mg/kg	< 78	< 78	< 78	< 78	185.98	150.71	< 78
Cu	mg/kg	61.28	65.33	61.63	57.29	61.31	56.55	49.14
Zn	mg/kg	102.60	124.29	114.33	124.88	114.26	111.91	128.73
Ga	mg/kg	39.38	42.54	35.01	57.33	52.46	30.87	39.00
Br	mg/kg	44.51	70.80	44.47	45.58	48.67	29.61	32.82
Rb	mg/kg	15.75	18.25	24.94	21.41	15.44	19.59	25.16
Sr	mg/kg	118.22	110.95	127.21	114.65	105.72	110.32	135.69
Y	mg/kg	36.47	33.69	39.53	40.70	35.81	29.04	37.41
Zr	mg/kg	470.34	459.50	570.78	421.66	464.32	839.88	713.83
Gd	mg/kg	495.08	< 145	349.87	< 145	392.58	< 145	440.56
Tb	mg/kg	1 813.82	1 457.69	1 977.18	2 005.54	1 625.05	1 705.97	1 668.44
Pb	mg/kg	37.46	33.88	36.47	46.59	35.73	27.25	41.27

Table 8. Average concentration of the elements in the analyzed soil samples (sample n°22 to sample n°28)

Elements	Unit	Sample 22	Sample 23	Sample 24	Sample 25	Sample 26	Sample 27	Sample 28
K	‰	3.69	3.76	3.50	2.77	6.96	4.19	3.77
Ca	‰	1.07	1.19	1.00	1.00	1.16	1.17	1.61
Ti	mg/kg	6 070.62	6 078.57	6 412.78	6 417.58	6 466.45	6 866.09	6 387.99
V	mg/kg	89.79	< 13	216.17	142.63	109.90	72.30	165.31
Cr	mg/kg	< 32	55.91	< 32	539.62	63.18	111.94	73.64
Mn	mg/kg	240.63	266.14	< 50	4 304.57	214.48	285.26	< 50
Fe	%	2.81	2.32	2.40	2.56	2.51	2.26	2.39
Co	mg/kg	< 78	167.29	220.64	< 78	< 78	< 78	< 78
Cu	mg/kg	53.96	48.91	52.01	49.54	60.51	50.02	46.43
Zn	mg/kg	134.03	124.04	122.41	107.97	139.29	115.32	120.30
Ga	mg/kg	45.44	33.28	45.84	38.24	47.22	43.93	40.97
Br	mg/kg	36.03	37.19	66.99	57.64	56.17	42.97	52.03
Rb	mg/kg	20.40	21.84	18.12	15.42	23.73	20.94	22.72
Sr	mg/kg	124.45	127.72	115.28	88.69	133.65	126.38	141.80
Y	mg/kg	36.71	34.12	37.47	32.61	35.80	39.79	33.25
Zr	mg/kg	426.29	457.97	411.28	319.71	517.07	587.85	603.71
Gd	mg/kg	< 145	397.07	< 145	< 145	< 145	371.40	376.34
Tb	mg/kg	2 034.88	1 513.27	1 582.86	1 583.16	1 608.47	1 802.16	1 698.17
Pb	mg/kg	50.53	43.76	40.39	38.63	38.46	35.01	39.35

Table 9. Average concentration of the elements in the analyzed soil samples (sample n°29 to sample n°35)

Elements	Unit	Sample 29	Sample 30	Sample 31	Sample 32	Sample 33	Sample 34	Sample 35
K	‰	4.92	5.93	3.73	4.02	3.00	2.41	3.32
Ca	‰	1.24	1.21	0.88	1.23	<DL	0.91	1.15
Ti	mg/kg	6 137.45	7 472.49	8 658.61	5 846.90	6 199.56	6 145.66	6 616.21
V	mg/kg	< 13	< 13	< 13	76.35	342.97	163.43	137.47
Cr	mg/kg	98.85	79.95	76.27	74.56	86.69	193.70	88.78
Mn	mg/kg	243.63	235.07	279.54	192.72	423.35	233.11	278.79
Fe	%	2.32	2.26	2.48	2.56	2.62	2.78	2.04
Co	mg/kg	171.37	< 78	< 78	193.89	127.71	< 78	< 78
Cu	mg/kg	< 11	60.54	44.79	40.89	65.86	47.30	58.66
Zn	mg/kg	117.27	128.29	134.70	138.71	122.93	117.03	107.97
Ga	mg/kg	33.77	48.23	43.67	43.15	46.11	41.38	34.09
Br	mg/kg	48.92	47.82	41.45	54.56	65.91	48.76	33.60
Rb	mg/kg	23.92	27.37	17.66	19.58	20.19	13.48	12.85
Sr	mg/kg	131.68	170.29	104.02	112.58	102.41	74.33	81.01
Y	mg/kg	39.23	42.78	30.96	29.16	36.61	32.26	25.47
Zr	mg/kg	529.26	755.91	466.69	432.28	501.78	553.05	367.91
Gd	mg/kg	< 145	< 145	< 145	384.90	454.99	< 145	< 145
Tb	mg/kg	1 864.58	1 715.60	1 665.61	1 690.00	1 628.28	2 081.64	1 653.91
Pb	mg/kg	38.05	45.58	35.98	42.37	48.41	43.43	26.96

The nutrient elements for the plant are classified as the following:

- principal constituent such as carbon (C), oxygen (O) and hydrogen (H);
- macroelements composed by calcium (Ca), magnesium (Mg) and sulfur (S) ;
- microelements or oligo-elements such as iron (Fe), manganese (Mn), zinc (Zn), bore (B), cooper (Cu), molybdenum (Mo) and chlorine (Cl) ;
- others elements like sodium (Na), selenium (Se), cobalt (Co), aluminum (Al) and silicon (Si) are essential for some plant (Mémento de l'Agronome, Décembre 2002).

The method soil pH in water was applied to determine the pH in the soil samples. The results showed that the concentration ranged between 4.30 and 5.19. It means that the study area was classified as acidic soil (Tom VELDKAMP, 1992).

For potassium (K), the results showed that the range concentrations varied from 1.8‰ to 7.79‰. It means the analyzed soils are rich in potassium because the concentrations are situated in the range from 1.5 to 2.3‰ (Mémonto de l'Agronome, 1991). Potassium was absorbed by the plant with an important quantity. It plays a role of regulator during the assimilation of the chlorophyll in the plant and improves the synthesis and accumulation of glucose. In addition, potassium permits the plants to economize water in the tissue and give them the higher rigidity and improve the capacity of the plant to resist to the different diseases (Mémento de l'Agronome, 4th edition, 1991). Finally, potassium was essential for the firmness of the plant cell (Tom VELDKAMP, 1992).

For calcium (Ca), the average concentration varied from 0.88 ‰ to 1.77 ‰. It means that analyzed soils are poor in calcium because the results are less than 2‰ (Mémonto de l'Agronome, 1991). Calcium plays an important role in term of physiology of the plant and it contribute mainly in the organization and stability of the structure of the plant (Maurice BONNEAU & Bernard SOUCHIER, 1st edition, 1994). It was called construction element (Tom VELDKAMP, 1992). For the sample n°33, the concentration of the calcium is below the detection limit.

For titanium (Ti), the range concentration varied from 4485 mg/kg to 8659 mg/kg. The results showed that the highest value is gain below the maximal concentration recommended in soil which is 10000 mg/kg and the lowest value is around the mean concentration of titanium recommended in soil which is 4000 mg/kg (Mémonto de l'Agronome, 1991). Therefore, we can conclude that there is no risk of toxicity for titanium in the study areas.

For vanadium (V), the concentration values of the following soil samples n°12, 13, 23, 29, 30 and 31are below the detection limit 13 mg/kg. For the other samples, the range concentration varied from 72 mg/kg to 343 mg/kg. We found that the highest concentration was below the recommended maximal concentration in soil 500ppm (Mémonto de l'Agronome, 1991). Then, we can conclude that there is no risk of the toxicity of the vanadium in the land of rice field Ambodivona.

Case of chromium (Cr), the obtained results showed that the mean concentration of chromium varied from 39 mg/kg to 540 mg/kg. We found that the highest concentration is below the recommended maximal concentration in soil 1000 mg/kg (Mémonto de l'Agronome, 1991).

Case of manganese (Mn), the concentration of manganese in the samples n°17, 24 and 28 are below the detection limit 50 mg/kg. But for the others samples, the range concentration varied from 179 mg/kg to 423 mg/kg. For the sample n°25, the measured concentration was higher than the recommended maximal concentration in soil 3000 mg/kg (Mémonto de l'Agronome, 1991). Then, the excess of manganese could be one of the factors which involves the toxicity of the soil and the deficiency of iron. Manganese plays a role important during the formation of chlorophyll, nitrate reduction and breathing of the plant and used as catalyst for metabolism. In addition, its absorption was improved by the aeration of soil with the presence of the iron (Mémonto de l'Agronome, 1991).

As for iron (Fe), the concentration fluctuated between 1.2‰ and 2.81‰. The results show that the lowest measured concentration is above the limit of the deficiency of iron in the soil 0.7‰ and the highest value is below the mean concentration accepted in soil 3.8‰ (Mémonto de l'Agronome, 1991). Therefore, we can conclude that the soil in the study areas contained sufficiently the iron. During the formation of chlorophyll, iron plays a role as catalyst. It moved slowly in the plant and his migration was promoted by the potassium (Mémonto de l'Agronome, 1991).

Case of cobalt (Co), the range concentration in the analyzed samples varied from 128 mg/kg to 221 mg/kg. In addition, the obtained results showed that the analyzed soil exceeded the deficiency limit of the cobalt in the soil 40 mg/kg (Mémonto de l'Agronome, 1991). But, there were some samples such as samples n° 2, 3, 5, 7, 8, 9, 10, 12, 13, 14, 15, 16, 17, 18, 21, 23, 25, 26, 27, 28, 30, 31, 34 and 35 which their concentrations were below the detection limit 78 mg/kg. Cobalt was essential for elaboration of the vitamin B12 (Mémonto de l'Agronome, 1991).

Case of cooper (Cu), for the samples n°8, 9, 10 and 29, the concentration of cobalt are below the detection limit 11 mg/kg. For the other samples, the concentration in the analyzed soil samples varied from 41 mg/kg to 67 mg/kg. We found that all values were above the accepted mean value of the cooper in the soil 30 mg/kg and the highest value was below the deficiency limit of the cooper in the soil 100 mg/kg. Then, we can conclude that the soil in the study areas was rich in cooper. Deficiency of the cooper in the soil involves the disease of the plant or irregularity of nutrient functioning. In the soil, cooper was presented in form total and exchangeable (Mémonto de l'Agronome, 1991).

Case of zinc (Zn), the mean concentration of zinc in the analyzed soil varied from 84 mg/kg to 139 mg/kg. All concentrations were upper the mean concentration acceptable and the maximum concentration was lower of the deficiency concentration limit. Then, we can conclude that the analyzed topsoil were rich in zinc (Mémonto de l'Agronome, 1991).

Case of gallium (Ga), the mean concentration of gallium in the soil varied from 25 mg/kg to 57 mg/kg. We found that the measured concentrations were situated between the mean concentration acceptable 14 mg/kg and the deficiency limit 70 mg/kg of the gallium in the soil.

Case of bromine (Br), the mean concentration measured in the samples varied from 27 mg/kg to 75 mg/kg. The results showed that all values were higher the deficiency limit of bromine in the soil 10 mg/kg.

Case of rubidium (Rb), the mean concentration of rubidium varied from 11 mg/kg to 29 mg/kg in the analyzed topsoil. All values were lower than the acceptable minimum limit in the soil 50 mg/kg. Then, we can conclude that the soil was poor in rubidium.

Case of strontium (Sr), the mean concentration varied from 50 mg/kg to 170 mg/kg. These values showed that the measured concentrations were lower than the mean acceptable value in the soil 200 mg/kg (Mémonto de l'Agronome, 1991).

Case of Yttrium (Y), the range concentration varied from 26 mg/kg to 43 mg/kg. In addition, the analyzed values were below the mean concentration accepted in the soil 50 mg/kg (Mémonto de l'Agronome, 1991).

Case of zircon, the analyzed concentration varied from 288 mg/kg to 840 mg/kg. The lowest value was around the accepted mean value 300 mg/kg and the highest concentration was lower than the maximum concentration acceptable in soil 2000 mg/kg (Mémonto de l'Agronome, 1991).

Case of gadolinium (Gd), fifteen samples contained sufficiently the gadolinium. Then, for the samples n° 8, n°9 and n°10, the concentrations were 4095 mg/kg, 4119 mg/kg, and 3929 mg/kg, respectively. The twelve samples varied from 309 mg/kg to 491 mg/kg. For the others samples, the measured concentrations were below the detection limit 145 mg/kg.

Case of terbium (Tb), the mean concentration varied from 1270 mg/kg to 2800 mg/kg. The concentrations of the sample n°8, n°9 and n°10 were upper 2000 mg/kg. For the others samples, the measured concentrations were below 2000 mg/kg.

Case of lead (Pb), the measured concentration varied from 24 mg/kg to 50 mg/kg. The results showed that these values were situated between the mean concentration 10 mg/kg and the maximum concentration accepted 200 mg/kg in the soil (Mémonto de l'Agronome, 1991).

V. Conclusion

The investigation in term of total elements in the soil in the rice field at Ambodivona in township Ambohitrimanjaka using Energy Dispersive X-ray Fluorescence (EDXRF) showed that the analyzed soil contained the useful elements for the plants such as potassium (K) and calcium (Ca). In addition, the soil contained some oligo-elements such as manganese (Mn), iron (Fe), cobalt (Co), cooper (Cu) and zinc (Zn) which are all nutrient elements for the plants. But, the soil in the study areas contained other elements not essential for the plant which are called undesirable elements such as titanium (Ti), vanadium (V), chromium (Cr), gallium (Ga), bromine (Br), rubidium (Rb), strontium (Sr), yttrium (Y), zircon (Zr) and heavy metal such as gadolinium (Gd), terbium (Tb) and lead (Pb). For the future work, the high concentration about bromine (Br), gadolinium (Gd) and terbium (Tb) in the soil will need a new investigation.

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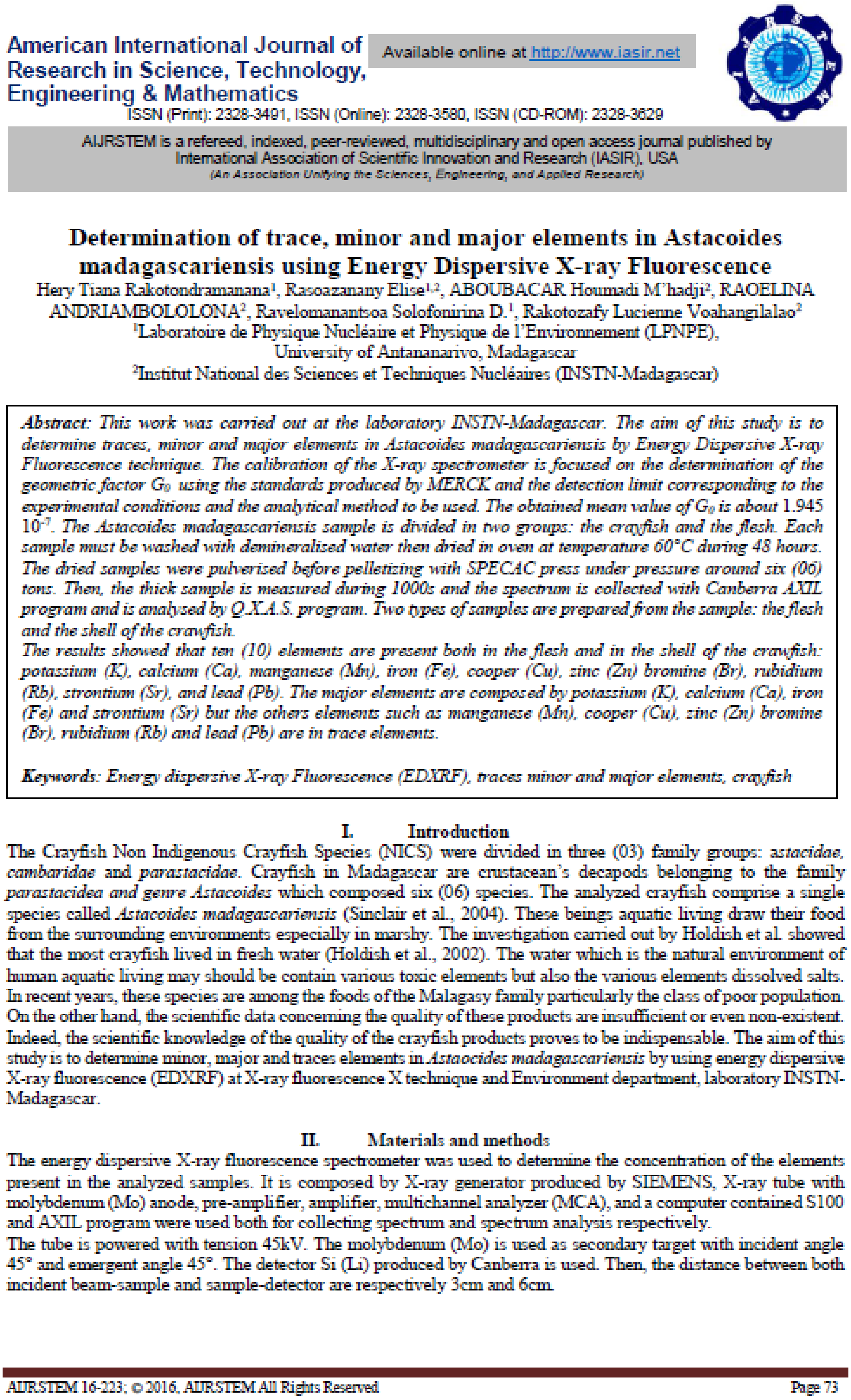

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Determination of trace, minor and major elements in Astacoides madagascariensis using Energy Dispersive X-ray Fluorescence

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Abstract: *This work was carried out at the laboratory INSTN-Madagascar. The aim of this study is to determine traces, minor and major elements in Astacoides madagascariensis by Energy Dispersive X-ray Fluorescence technique. The calibration of the X-ray spectrometer is focused on the determination of the geometric factor* G_0 *using the standards produced by MERCK and the detection limit corresponding to the experimental conditions and the analytical method to be used. The obtained mean value of* G_0 *is about* 1.945 10^{-7}. *The Astacoides madagascariensis sample is divided in two groups: the crayfish and the flesh. Each sample must be washed with demineralized water then dried in oven at temperature 60°C during 48 hours. The dried samples were pulverised before pelletizing with SPECAC press under pressure around six (06) tons. Then, the thick sample is measured during 1000s and the spectrum is collected with Canberra AXIL program and is analysed by Q.X.A.S. program. Two types of samples are prepared from the sample: the flesh and the shell of the crawfish.*

The results showed that ten (10) elements are present both in the flesh and in the shell of the crawfish: potassium (K), calcium (Ca), manganese (Mn), iron (Fe), cooper (Cu), zinc (Zn) bromine (Br), rubidium (Rb), strontium (Sr), and lead (Pb). The major elements are composed by potassium (K), calcium (Ca), iron (Fe) and strontium (Sr) but the others elements such as manganese (Mn), cooper (Cu), zinc (Zn) bromine (Br), rubidium (Rb) and lead (Pb) are in trace elements.

Keywords: *Energy dispersive X-ray Fluorescence (EDXRF), traces minor and major elements, crayfish*

I. Introduction

The Crayfish Non Indigenous Crayfish Species (NICS) were divided in three (03) family groups: *astacidae, cambaridae* and *parastacidae*. Crayfish in Madagascar are crustacean's decapods belonging to the family *parastacidea and genre Astacoides* which composed six (06) species. The analyzed crayfish comprise a single species called *Astacoides madagascariensis* (Sinclair et al., 2004). These beings aquatic living draw their food from the surrounding environments especially in marshy. The investigation carried out by Holdish et al. showed that the most crayfish lived in fresh water (Holdish et al., 2002). The water which is the natural environment of human aquatic living may should be contain various toxic elements but also the various elements dissolved salts. In recent years, these species are among the foods of the Malagasy family particularly the class of poor population. On the other hand, the scientific data concerning the quality of these products are insufficient or even non-existent. Indeed, the scientific knowledge of the quality of the crayfish products proves to be indispensable. The aim of this study is to determine minor, major and traces elements in *Astaocides madagascariensis* by using energy dispersive X-ray fluorescence (EDXRF) at X-ray fluorescence X technique and Environment department, laboratory INSTN-Madagascar.

II. Materials and methods

The energy dispersive X-ray fluorescence spectrometer was used to determine the concentration of the elements present in the analyzed samples. It is composed by X-ray generator produced by SIEMENS, X-ray tube with molybdenum (Mo) anode, pre-amplifier, amplifier, multichannel analyzer (MCA), and a computer contained S100 and AXIL program were used both for collecting spectrum and spectrum analysis respectively.

The tube is powered with tension 45kV. The molybdenum (Mo) is used as secondary target with incident angle 45° and emergent angle 45°. The detector Si (Li) produced by Canberra is used. Then, the distance between both incident beam-sample and sample-detector are respectively 3cm and 6cm.

II.1. Calibration and method quality control

a) *Calibration*

The goal of the calibration is to determine the mean geometrical factor G_0. This constant permit to calculate the fluorescence intensity for each j element in the sample by the following general formula:

$$I_j = G_0 K_j \rho_j d T_j$$

with

G_0 : mean geometrical factor

K_j : relative efficiency excitation-detection for j element

T_j : transmission coefficient or absorption correction factor

ρ_j : sample density

d : sample thickness

For thick sample, the following formula is used:

$$I_j = G_0 K_j \frac{1}{a_j} C_j$$

with

C_j : concentration for j element

a_j : absorption coefficient for j element

Then, the calibration of the X-ray spectrometer is carried out by using the standard produced by MERC. They are composed by potassium chloride (KCl), calcium oxyde (CaO), ferrous sulfate anhydride ($Fe\ SO_4$, $7H_2O$) (FeO), cooper oxyde (CuO), zinc oxyde (ZnO), potassium bromide (KBr), strontium carbonate ($SrCO_3$) and lead dioxides (PbO_2).Thick samples are prepared from these standard powder. Then, they are measured during 1000s. Experimental measurement permits to obtain the geometric factor for each element and the mean geometric factor was in order of 1.945x10^{-07}. Table 1 gives the corresponding results:

Table 1: Mean and individual constant geometrical factor for each standard

Elements	Individual Constant G_0
K	1.905x10^{-7}
Ca	1.980x10^{-7}
Fe	1.970x10^{-7}
Cu	1.900x10^{-7}
Zn	1.940x10^{-7}
Br	1.980x10^{-7}
Sr	2.001x10^{-7}
Pb	1.881x10^{-7}
Mean	1.945x10^{-7}

b) *Method Quality control*

The Certified References Materials (CRM) codified IAEA-407 and IAEA-436 are used for method quality control. IAEA-407 is made by fish tissue and IAEA-436 is prepared from tuna fish flesh.

The comparison of the experimental results conducted at the Madagascar INSTN and certified the IAEA values referred respectively in table 2 and table 3 for the CRM IAEA-407 and CRM IAEA-436

Table 2: Comparison of the results measured at INSTN-Madagascar and the certified values IAEA-407

Elements	Unit	IAEA-Certified values	INSTN-Madagascar results	Percentage difference (%)
K	mg.kg^{-1}	13.1	14.1 ±0.8	7.63
Ca	mg.kg^{-1}	27.0	27.5 ±1.1	1.85
Mn	mg.kg^{-1}	3.52	3.62 ±0.60	2.76
Cu	mg.kg^{-1}	3.28	3.48 ±0.40	5.74
Zn	mg.kg^{-1}	67.1	68.4 ±0.6	1.94
Br	mg.kg^{-1}	94.0	94.7 ±0.7	0.77
Rb	mg.kg^{-1}	2.86	3.02 ±0.56	5.29
Sr	mg.kg^{-1}	130	128.2 ±0.5	1.38

Table 3 : Comparison of the results measured at INSTN-Madagascar and the certified values IAEA-436

Elements	Unit	IAEA-Certified values	INSTN-Madagascar results	Percentage difference (%)
K	mg.kg^{-1}	12.3	12.1 ±0.6	1.63
Ca	mg.kg^{-1}	154	152.0±2.0	1.30
Mn	mg.kg^{-1}	0.238	0.240 ±0.05	0.42
Cu	mg.kg^{-1}	1.73	1.65 ±0.10	4.62
Zn	mg.kg^{-1}	19.0	18.40 ±1.3	3.15
Br	mg.kg^{-1}	14.8	14.5 ±1.00	2.02
Rb	mg.kg^{-1}	2.41	2.24 ±0.50	7.05
Sr	mg.kg^{-1}	0.564	0.562 ±0.3	0.35