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## Destructive and Nondestructive Analysis of Some Modern Coins using ICP-AES and PIXE Techniques

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**Abstract** In this work, The ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) and PIXE (Proton Induced X-ray Emission) techniques were used to determine the elemental compositions of some modern coins. The coins of interest were (250, 500LL) Lebanese Lira coins, (50, 100PT) Egyptian coins and (2€) Euro coin. The study showed that the most forming composition in these coins are ten elements namely, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ti, Al and V. For Lebanese Lira coins (250 and 500LL), both (Cu and Fe) are the main structural elements whereas Al, Zn and Ni are present as a minor elements. For the 100PT Egyptian and 2 € coins, both Cu and Ni are found to be the main structural elements while Zn and Fe are the minor elements and all other elements are present in the trace level. The ICP-AES showed greater sensitivity for the analyses of coins, especially for trace elements indicating that PIXE is probably not the most accurate technique to determine the absolute concentration of trace elements.

**Keywords** PIXE, ICP-AES techniques, Coins, Destructive, Non-destructive, Quality control

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### 1. Introduction

Elemental analysis has received more attention with the rapidly increasing industrial development in the second half of the twenty century, and the responsibility for securing high quality standards for industrial products in particular as well as for quality of life in general. The development of analytical methods has led to detect elements in very low concentrations [1].

Nuclear/atomic physical methods have been developed to determine the elemental composition, mainly X-ray fluorescence (XRF) [2], Neutron Activation Analysis (NAA) [3], Proton Induced X-ray Emission (PIXE) and both inductive coupled plasma atomic emission and mass spectrometry (ICP-AES/MS) [4,5]. The use of ion beam analysis techniques (IBA) [6] has grown recently since they combine the advantages of being non-destructive and multi-elemental high-sensitivity analytical techniques. They can be used individually or in combination with other techniques to obtain a large number of information and detailed data for the system being studied.

ICP-AES and PIXE are widely used in analytical methods to determine the elemental composition and concentrations for soils, sediments, aerosols and other environmental samples. Both analytical methods have yielded accurate and precise measurements in wide a range of applications and under varying conditions (*i.e.*, sample size requirements and availability, sample preparation technique, range of elements, etc [7-13]. The inter-comparison of elemental composition / concentrations obtained by two or more analytical techniques is important for quality



control and quality assurance purposes [14]. It is understood that some methods are more suitable for measuring higher concentrations whereas others are more precise in measuring low concentrations [9].

Proton Induced X-ray Emission (PIXE) is an X-ray spectrographic technique, which can be used for the non-destructive, simultaneous elemental analysis of solid, liquid or aerosol filter samples. PIXE can be used to measure virtually every element from Na to U in the periodic table. PIXE is comparatively universal, i.e. applicable to many materials and objects of any dimension. Among various non-destructive methods of analysis such as EDXRF, PIXE and electron probe microanalysis (EPMA), the PIXE technique is of special interest for the analysis of coins because it is not only non-destructive but also fast, sensitive and capable of simultaneous multi-elemental analysis [15]. The PIXE technique using protons of energy 1–3MeV has an analytical depth of about 35 mm due to the limited range of protons. Heavy elements in this case are detected by the LX-rays in the spectra at high energy PIXE, because of the use of higher energy and hence higher crosssection, the heavy elements can be detected via KX-rays [16].

The ICP-AES spectrometer was used for elemental analysis in the trace and ultra-trace range; it is a multi-elements analysis (73 elements)[17, 18]. It shows detection limits between 0.1-10.0 ppb for most elements, and the sample consumption is between 3-15 ml / sample. The sample introduced into the ICP-AES must usually contain less than 0.1% dissolved solids to prevent salt buildup. ICP-AES also has the ability to determine a wide range of elements and is used for the determination of low atomic number elements such as Na and Mg [9]. ICP-AES and PIXE have been used by numerous investigators to complement one another where ICP-AES is used for the determination of low atomic number elements and PIXE for the determination of elements having atomic numbers larger than Na [19].

This work aims principally to utilize PIXE and ICP-AES techniques for the determination of elements in some selected coins which is a characterization study in the field of quality control and verification of the actual elemental composition of materials under investigation.

## 2. Experimental

The proton beam used in the present study was obtained from Al Phatross RF ion source at a tandem Pelletron accelerator from NEC of 1.7 MV, model 5-SDH[20]. The spot diameter of the beam on the target was about 2mm, defined by a Ta anti-scatter collimator. The multi-purpose scattering chamber, 30cm diameter, is designed to carry out PIXE, RBS (Rutherford back scattering spectroscopy) and PIGE (proton induced gamma ray), where the beam hits the target under normal incidence. The chamber contains X-ray detector and is equipped with a rotating wheel target holder (up to 16 samples) monitored by PC through a stepping motor. X-ray emission from targets is detected using an OrtecSi (Li) detector (SLP-06165 model) with 30 mm<sup>2</sup> active area, 12.7 μm thick Be window, and 170eV measured FWHM energy resolution at 5.9 keV, placed at 135<sup>0</sup> to the beam direction. The elemental composition of the samples was measured by the conventional in vacuum PIXE, using the accelerator facility at the Lebanese Atomic Energy Commission. Figure 1 shows the accelerator facility at the Lebanese, Atomic Energy Commission and an image of the IBA principles.

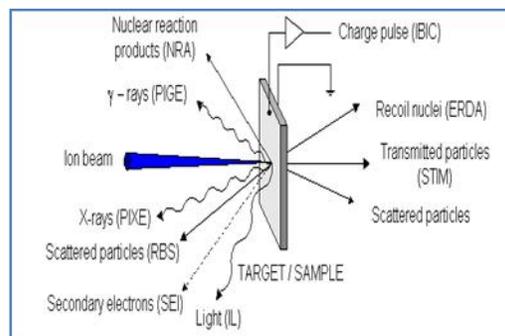


Figure 1: Accelerator facility at the Lebanese Atomic Energy Commission and an illustration of the IBA technique



PIXE spectra were processed with the Gupix package (Guelph PIXE software package). This program is based on the fundamental parameter approach including X-ray production cross-sections, X-ray attenuation coefficients, proton stopping powers, detector efficiency, collected charge and geometry effects to produce an output of elemental concentrations in ppm.

For ICP-AES; JY 138 instrument supplied from JOBIN-YVON France, sequential spectrometer, which is installed at the Chemical Laboratory in Second Research Reactor at the Nuclear Research Center of the Atomic Energy Authority of Egypt was used. The working conditions of ICP-AES are summarized in Table (1).

**Table 1:** Operating conditions for ICP-AES instrument

Parameters	Values
Power	1.1 Kw
Outer gas flow rate	14.0 l/min
Auxiliary gas flow rate	0.2 l/min
Carrier gas flow rate	1.0 l/min
Observation height	15.0 mm
Sample feed rate	1.4 ml/min

Usually, SRM DR-N, and SRM 871 from NIST are routinely used to calibrate the experimental set-up for PIXE and the SRM (SIGMA) of each element are used to calibrate ICP-AES. Figure 2 shows the studied coin samples where the (250 and 500 LL) Lebanese coins, the (50 and 100PT) Egyptian coin and (2€) euro coin are presented.

For PIXE and ICP-AES analysis, the coins were cleaned by ultrasonic cleaner using 2% nitric acid in deionized water for 10 minutes, and then dried with air streaming for 20 min to remove any dust from the surface. For ICP-AES; a part of these coins was cut, weighted and dissolved in aqua regia then filled to take the desired volume.



*Figure 2: The photograph of both sides of the analyzed coins: 250-LL, 500-LL, 50 PT, 100 PT (disk and ring) and 2€.*

There is no definite classification of what are the percentages of the major, minor and trace elements. In this study, we considered the concentration of the major elements are up to 1%, minor elements are between 0.1% and 1%, and trace elements are those below ( $< 0.1\%$ ).

### 3. Results and Discussion

#### 3.1. Analysis of (250 and 500 LL) Lebanese Lira Coins

PIXE and ICP-AES techniques were used to determine all concentrations of major, minor and trace elements in (250 and 500 LL) Lebanese coins. The chemical composition of these coins was listed in Table (2).

For 250 LL, ten different elements namely, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ti, Al and V were found using the ICP-AES technique while only five elements namely, Ni, Fe, Zn, Cu and Al were detected by PIXE technique. Cu was the main element with a concentration of 86.53% and 88.52 using ICP-AES and PIXE respectively. The other



major elements detected in this coin were Al, Zn and Ni while Fe was detected as minor element in both techniques. The results show also that all the trace elements detected by ICP-AES were not detected by the PIXE technique. This may be due to the detection limits of PIXE which is lower than ICP-AES [21]. For 500LL, the obtained results show that the coin was mainly formed from Fe with a concentration of 93.04% and 97.94% using ICP-AES and PIXE technique respectively. The major elements of the 500LL were Fe and Ni while Mn was a minor element and other elements were in the trace level. Generally, the measurements of PIXE basically have similar results with that obtained from the ICP-AES especially in case of major and minor elements. The error in the results of the major and minor elements between PIXE and ICP-AES techniques is <10%.

**Table 2:** Elemental composition of 250 and 500LL as determined by ICP-AES and PIXE

Elements	250LL		500LL	
	ICP-AES	PIXE	ICP-AES	PIXE
	wt %	wt %	wt %	wt %
Cr	0.09	nd	0.04	nd
Ni	1.40	1.59	2.65	3.32
Co	0.01	nd	0.004	nd
Fe	0.19	0.22	93.04	96.49
Mn	0.05	nd	0.12	0.19
V	0.02	nd	nd	nd
Cu	86.53	88.52	0.04	nd
Zn	3.65	4.17	0.02	nd
Ti	0.005	nd	0.08	nd
Al	4.74	5.50	0.04	nd

nd = non detectable

### 3.2. Analysis of (50 and 100PT) Egyptian Coins

The 100PT Egyptian coin is mainly consisting of two parts one of them is a ring and the other is a desk. ICP-AES and PIXE techniques were used to determine all elements composition of (50 and 100PT). Egyptian coins under the same conditions of the previously studied coins. The data are shown in Table (3).

Analysis of the 100PT (ring and desk parts) using ICP-AES shows the presence of nine elements namely (Cr, Mn, Fe, Ni, Cu, Zn, Ti, Al and Co). The obtained results using PIXE show that (Ni, Fe, Cu and Zn) and (Ni, Fe, Mn, Cu and Zn) were detected for the ring and desk parts respectively.

**Table 3:** The elemental composition of 100 Pt. (Ring), 100 Pt. (Desk) and 50Pt. measured by ICP-AES and PIXE (wt%)

Elements	100PT (Ring)		100PT (Desk)		50 PT	
	ICP-AES	PIXE	ICP-AES	PIXE	ICP-AES	PIXE
	wt %	wt %	wt %	wt %	wt %	wt %
Cr	0.05	nd	0.02	nd	0.02	nd
Ni	23.40	25.57	3.11	4.13	3.02	3.51
Co	0.01	nd	0.003	nd	0.003	nd
Fe	3.15	3.89	2.43	3.48	4.66	6.22
Mn	0.02	nd	0.14	0.24	0.15	0.27
V	nd	nd	nd	nd	nd	nd
Cu	59.87	62.78	69.3	72.77	64.92	63.37
Zn	5.09	7.76	17.9	19.38	23.43	26.63
Ti	0.08	nd	0.001	nd	0.002	nd
Al	0.09	nd	0.03	nd	0.03	nd



In case of 50PT Egyptian coin, nine elements (Cr, Mn, Fe, Ni, Cu, Zn, Ti, Al and V) were found using ICP-AES while only five elements (Ni, Fe, Mn, Cu and Zn) were found using PIXE. The data of Table (3) reveal that the copper is the main element of 50 and 100pt (for ring and desk). So, the Egyptian coins are mainly consisting of copper with zinc or nickel as the second major element. According to ICP-AES results, the major elements in case of 100PT ring are Cu (59.87%) and Ni (23.40%), Zn (5.09%) and Fe (3.15%) whereas the remaining elements were in the trace level. In case of 100PTdesk, the major elements were Cu (69.3%), Ni (3.11%), Fe (2.43%) and Zn (17.9%) whereas Mn (0.14%) was a minor element and other remaining elements were in the trace level. In case of 50PT Egyptian coin, the major elements are Ni (3.02%), Fe (4.66%), Cu (64.92%) and Zn (23.43%) whereas Mn (0.15 %) was a minor element and other remaining elements were in the trace level. Regarding to PIXE measurements, (the 100PT ring), the major elements were Cu (62.78%) and Ni (25.57%), Zn (7.76%) and Fe (3.89%) while the trace elements were not detected. Also, the major elements in case of 100PT desk are Cu (72.77%), Zn (19.38%), Ni (4.13%), and Fe (3.48%) while Mn (0.24%) was in a minor level, the trace elements were not detected. According to PIXE measurements in case of 50PT, the major elements were Cu (63.37%), Zn (26.63%), Fe (6.22%) and Ni (3.51%) while Mn (0.27%) was in a minor level. All the trace elements were not detected in this coin sample. Generally, the obtained results between the PIXE and ICP-AES were in good agreement for major and minor elements.

### 3.3. Analysis of (2 €) Euro Coin

The results of elemental analysis of 2 Euro coin sample using ICP-AES and PIXE techniques are given in Table (4). Eight elements (Cr, Ni, Co, Fe, Mn, V, Cu and Zn) were detected by ICP-AES while only five elements (Ni, Fe, Mn, Cu and Zn) were detected by PIXE technique. Cu and Ni are the main elements composing the 2 € coin using ICP-AES and PIXE techniques. The results of the detected elements are presented in Table (4). The obtained results show a satisfactory agreement between the two techniques for major and minor elements while there is no evidence for the presence of the trace elements using PIXE technique. These results are in good agreement with ref. [20].

**Table 4:** The elemental analysis measured by ICP-AES and PIXE for 2€ coin

Elements	2 € coin	
	ICP-AES wt %	PIXE wt %
Cr	0.01	nd
Ni	13.98	19.82
Co	0.01	nd
Fe	0.05	0.07
Mn	0.10	0.11
V	0.001	nd
Cu	70.89	74.99
Zn	3.05	4.98
Ti	nd	nd
Al	nd	nd

### 3.4. Comparison between PIXE and ICP-AES

Figures 3 and 4 show the chemical composition for all of the studied coins measured by ICP-AES and PIXE respectively. In most cases, the results show that the values of the major elements of coins in both techniques were within the experimental error. In most cases, PIXE revealed higher concentrations of the elements than ICP-AES especially in case of major and minor elements except in case of Cu in 50PT ring; these results are in strongly agreement with ref. [22]. In contrast, in case of trace elements, most of the elements were detected by ICP-AES but not detected by PIXE technique. This may be due to the following:

(1): the detection limits of two techniques, for ICP-AES the detection limits are between 0.1-10.0 ppb for most of the elements but the detection limits of PIXE are of the order of 1 ppm for most of the elements. Detection limits (DLs) for PIXE are established on a per sample basis and are dependent upon the atomic number, matrix



interferences, detector efficiency, proton beam intensity and irradiation time, For elemental determination by PIXE, special attention is focused on the detection of low atomic number elements, normally described in the literature as elements in the  $Z \leq (11)$  Na range. Most PIXE analyses are not sufficiently sensitive to detect or quantify elements of  $Z \leq (11)$  [7, 23-25]. Although ICP-AES and PIXE also have measuring capability of elements from Na to U in the periodictable, but the best suited for elements is in the medium atomic number ( $Z$ ) in the range  $19 < Z < 31$  [26]. Other possible drawbacks are that the detection limits of PIXE are generally higher than those for ICP-AES and the lack of homogeneous material might produce skewed results [12]. In this study, the atomic numbers of the studied elements were in the range ( $Z= 22-30$ ) except Aluminum, ( $Z=13$ ), so most of the detected elements lie in the suitable range of detection limits of PIXE.

(2): Differences in analytical conditions and sample preparation, the sample preparation and condition may be causing some errors spatially in case of trace levels.

(3): Cross-contamination from instruments [23]. As a conclusion, this work shows that ICP-AES and PIXE are complementary techniques and their combined use is able to give powerful information about the chemical composition of metals in the coins. This conclusion of this work is in highly agreement with the results of ref. [27].

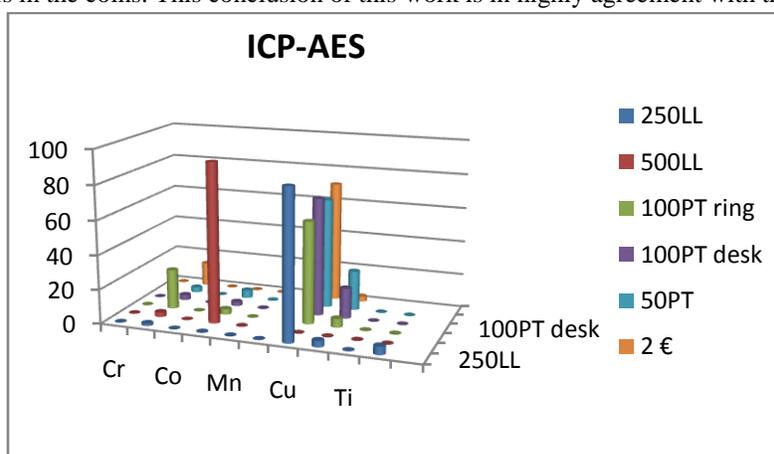


Figure 3: Elemental analysis of all studied coins determined by ICP-AES technique

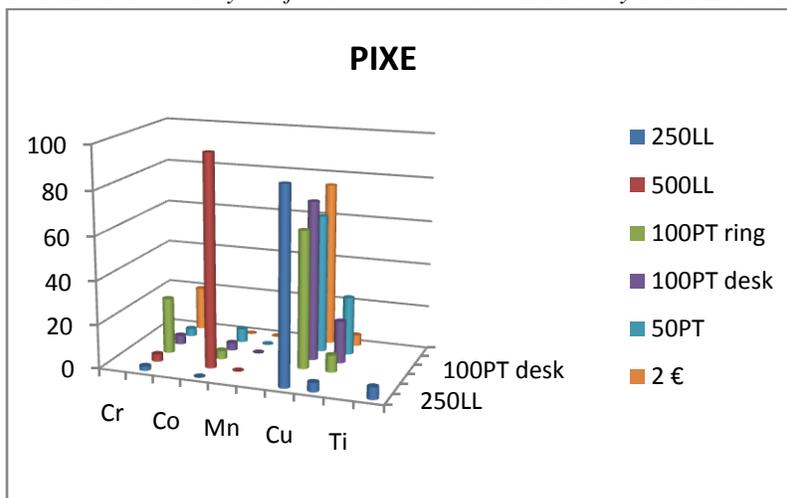


Figure 4: Elemental analysis of all studied coins determined by PIXE technique

#### 4. Conclusion

Two analytical techniques namely ICP- AES and PIXE were used to identify and quantify the elemental composition of coin samples. Considering the concentrations of the major and minor elements detected slight



difference between the two techniques was observed, this difference lies within the estimated experimental error between the two techniques. The obtained results show that the ICP-AES is more convenient for detecting the trace elements present in the samples. All the trace elements detected by this technique were not identified on using PIXE. On the other hand since PIXE is a non-destructive technique it is very useful to be used whenever we need a non-destructive analysis. Finally we can conclude that PIXE and ICP-AES are a complementary techniques and their combined use is able to give a trustable data on the chemical composition and the concentration of the metals forming the analyzed samples.

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