

EVALUATION OF INTERELEMENT EFFECTS OF Ag – Cu – Ti TERNARY SYSTEM BY X-RAY FLUORESCENCE TECHNIQUE

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Abstract

The interelement effects of Ag-Cu-Ti Ternary system was studied by x-ray fluorescence to obtain the concentration of each element accurately. Ternary compacted of high pure metals of Ag-Cu-Ti as a green pellets were prepared. Wavelength dispersive technique was used to measure the fluorescent intensities of ternary system at the same operation condition. The intensities of the ternary elements in the spectrum were non-linearly related to concentration of each element due to the absorption and enhancement effects. Ag absorbs x-ray fluorescence of Ti more than Cu. Binary influence coefficients were obtained from the values of relative intensities to calculate the elemental concentration of ternary system using BB (Bettie – Berssey) algorithm.

Keywords: X-ray, ternary effect, fluorescence, elementary analysis.

Introduction

X-rays are electromagnetic radiation of short wavelength in the range 0.1-10 Å. X-ray fluorescence (XRF) technique has become widely accepted as a multi-element analytical method for qualitative and quantitative analysis of elements [1]. XRF technique provided important tool for the identification and classification of materials for industry and research [2]. XRF analysis involves creation of vacancies in inner shells of an atom by X-ray photons, and the subsequent measurement of the fluorescent X-rays emitted when the vacancies fill from outer shells. When a monochromatic beam of X-ray photons fall onto a specimen, some are scattered, some are absorbed, and some pass through the specimen unaffected (transmitted). The absorbed part of the X-ray beam gives rise to fluorescent X-ray. Since the atomic number of an element in the specimen is related to the wavelength emitted by that specimen (Moselys law), therefore measuring the wavelength of a particular characteristic line allows the identification of an element, while intensity measurement of the same line is directly related to the concentration of that element[3,4]. Specimen irradiation procedure involves a number of experimental errors. Source-sample-detector geometry could have negative contribution to the results if the geometry is not chosen properly [5, 6, 7]. Other sources of errors is the specimen nature and the interelement effects [8, 9].

Theory

Primary fluorescence results from the direct effect of the incident beam on the element considered. The secondary fluorescence is often associated with an element of high atomic number than that of fluorescent element. Ternary fluorescence caused from the secondary fluorescence of an element induces a ternary fluorescence of another element in the same sample [9]. For multi-elements sample, the interfering effects are present, and the fluorescent intensity can depart widely from the effect of each element in a sample. Three types of effect are present, absorption effect, enhancement effect and third element effect [10]. After intensity correction for background, the ratio of intensities for a given line from the sample and pure standard element is directly proportional to the weight per unit area of the element in the specimen being analyzed [11, 12].

Let (I_i) be the intensity of the characteristic line from element(i) in the sample and (I_{pi}) be the intensity of that line from pure element (i). Then if (W_i/a) is the weight (W) per unit area (a) of the element (i) in the sample. Then intensity-weight relationship can be written as:

$$I_i / I_{pi} = W_i / a \dots \dots \dots (1)$$

Since, for three component mixture:

$$W_i + W_j + W_k = 100\% = 1 \dots \dots \dots (2)$$

where i, j and k are elements in sample [4, 5].

$$R_i = I_i / I_{pi} \text{ relative intensities..... (3)}$$

Bettie- Berssey (BB) were the first to suggest that in a limited range of composition, the interelement effects could be represented by the equation [8, 11]:

$$C_i / R_i = C_i + K_{ij} C_j + K_{ik} C_k..... (4)$$

where C_i , C_j and C_k are concentration of elemental i, j, k respectively in a sample. K_{ij} and K_{ik} are influence coefficients of elements j, k on element i.

and equation (3) can be written as:

$$K_{12} = C_1 / C_2 (1/R_1 - 1) (5)$$

$$K_{21} = C_2 / C_1 (1/R_2 - 1) (5)$$

Solution of these equations for each binary system led to the influence coefficients of Kth values [8, 11].

Experimental

Compacted filler of Ag, Cu and Ti was prepared for this investigation. Powders of pure Ag, Cu and Ti were compacted in different concentration as shown in Table (1)

and carefully mixed by three dimension automatic mixer machine to obtain homogeneity.

Two sets of compacted pellets were prepared as a ternaries elements for the (XRF) technique requirements. First set was composed of pure elements of Ag, Cu and Ti as a standard element pellets. Second set was composed of elements of Ag, Cu and Ti in different concentration as mentioned in Table (1). A stainless steel die of inner diameter equal to 8.65 mm was used to compact a green cylindrical pellet using hydraulic press (STRUERS type) with pressure of 15 kN. Wavelength dispersive spectrometer (WDS) technique of (Siemense type)-SRS-200 sequential was used for quantitative analysis of the prepared compacted powders with operation condition of 33 kV and 25 mA.

*Table (1)
Prepared compacted green pellets.*

<i>Sample no.</i>	<i>Total weight</i>	<i>Silver wt%</i>	<i>Copper wt%</i>	<i>Titanium wt%</i>
1	0.2 gm	100	–	–
2	0.2 gm	–	100	–
3	0.2 gm	–	–	100
4	0.2 gm	72	28	0
5	0.2 gm	65	35	2
6	0.2 gm	68	28	4
7	0.2 gm	55	37	8

Results and Discussion

The count rates of compacted samples as a function of concentration is stated in Table (2).

The concentration (C) and relative intensities R is deduced from the intensity values due to (XRF) technique stated in Table (3) for a compacted green pellets of AgCuTi.

Table (2)
Represent the compacted pellets after analyzed by XRF technique.

Sample no.	Silver		Copper		Titanium	
	C (wt%)	Count rate	C (wt%)	Count rate	C (wt%)	Count rate
1	100%	23150	–	–	–	–
2	–	–	100	11750	–	–
3	–	–	–	–	100	2350
4	65	16137	35	3460	0	–
5	70	14725	30	2400	0	–
6	75	17100	25	2045	0	–
7	71	16090	28	2400	1	30
8	63	14300	35	3700	2	35
9	75	16680	22	2200	3	39
10	68	16500	28	2305	4	95
11	55	14850	37	2850	8	207
12	50	13450	40	3000	10	390

Table (3)
Represent the relative intensities as a function of real concentration.

Sample no.	Ag			Cu			Ti		
	R	C%	C/R	R	C%	C/R	R	C%	C/R
1	1	100	1	0	0	0	0	0	0
2	0	0	0	1	100	0	0	0	0
3	0	0	0	0	0	0	1	100	1
4	0.7	65	0.93	0.31	35	1.13	0	0	0
5	0.636	70	1.1	0.216	30	1.39	0	0	0
6	0.736	75	1.02	0.187	25	1.33	0	0	0
7	0.696	71	1.02	0.216	28	1.29	0.013	1	0.77
8	0.618	63	1.02	0.32	35	1.09	0.0154	2	1.3
9	0.717	75	1.04	0.193	22	1.14	0.0184	3	1.63

The (R) versus (C) of each compacted constituent were plotted as shown in Fig.(1). The figure reveal that both Ag and Ti shows a non-linear relation between (R) and their (C) values. But the R-C value correlation for copper constituent is almost a parabolic

correlation. This could be interpreted because Ag absorbs Ti X-ray fluorescence more than of X-ray fluorescence of Cu. This calibration curve was used to compare between the real and calculated concentration of the compacted filler when used as an alloy filler. X-ray

intensity of Ag fluorescence is increased when the fluorescent intensity of both Cu and Ti are decreased. The main reasons are, the elements constituents have different electron density, then it differs in mass absorption coefficients. As a result, the involved complex absorption coefficients such as μ_i , μ_j , and μ_k can not be considered as constants, even with fixed excitation conditions, but as quantities also varying with the specimen compositions. According to this fact, the interelement effect is present and play an important role in X-ray

absorption and enhancement effects and their combinations. Since, the lighter elements yield significantly lower intensities so that, by increasing the counting period to reduce the effect of the counting statistics, the influence on the evaluation of the coefficient remains. In order to correct the experimental results due to absorption effect, the BB algorithm is employed as follows:

Solution of double equations (5) is given by Table (4).

Table (4)
Represent the influence coefficients values of binary elements.

Fluorescent element <i>i</i>	Interfering element		
	Ag	Cu	Ti
Ag	–	0.796	3.62
Cu	1.198	–	11.21
Ti	1.004	1.256	–

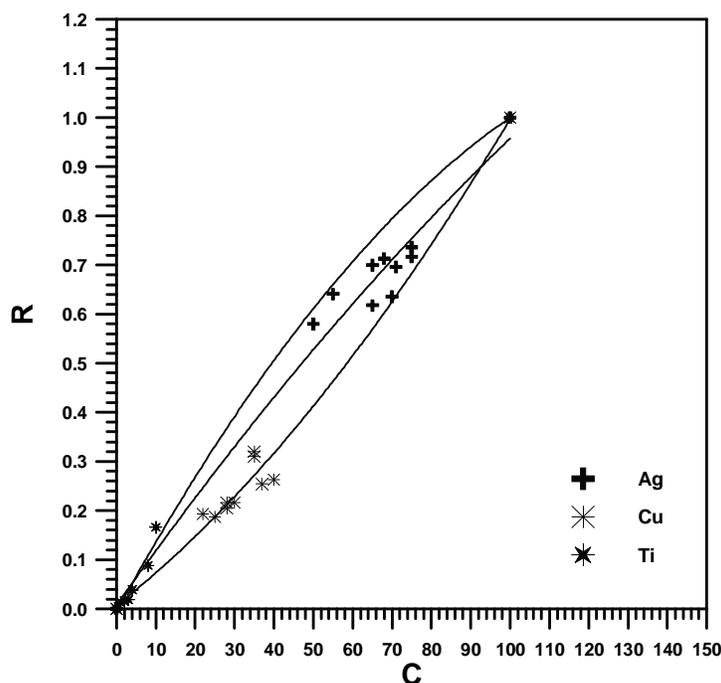


Fig. (1): Represent the relative intensity versus the concentration.

From the values of K coefficients the calculated concentration would be obtained

for the ternary elements Ag – Cu – Ti as in Table (5).

Table (5)
Comparison between the real and calculated concentrations with their relative errors for Ag- Cu – Ti binary and ternary elements.

<i>Element</i>	<i>Standard Concentration %</i>	<i>Calculated Concentration %</i>	<i>Relative Error %</i>
Ag	75	75.5	0.66
Cu	25	24.2	-3.2
Ti	0	0	0
Ag	70	70.2	0.28
Cu	30	29.5	-1.66
Ti	0	0	0
Ag	65	64.5	-0.77
Cu	35	35.2	0.57
Ti	0	0	0
Ag	71	70.3	-0.98
Cu	28	28.4	1.43
Ti	1	1.1	10.0
Ag	63	63.2	0.317
Cu	35	34.2	-2.28
Ti	2	2.3	15
Ag	75	74.1	-1.2
Cu	22	22.2	0.91
Ti	3	3.4	13.3
Ag	68	67.2	-1.17
Cu	28	28.3	1.07
Ti	4	4.4	10
Ag	55	55.2	0.36
Cu	37	36.5	-1.35
Ti	8	8.2	2.5
Ag	50	50.5	1.0
Cu	40	39.6	-1.0
Ti	10	10.2	2.0

Conclusion

- 1- Due to the presence of interelement effects, the absorption and enhancement effects played significant role in the relationship between the real and calculated concentrations.
- 2- BB algorithm is considered sufficient treatment to correct the calculated

concentration and to reduce the resultant errors.

- 3- Intensities of light elements are increased due to the presence of interelement effects and more precisely enhancement effects from heavier elements.

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الخلاصة

درست التأثيرات البينية للنظام الثلاثي فضة- نحاس- تيتانيوم بواسطة تقنية الاشعة السينية المتفلورة للحصول على تراكيز العناصر المكونة للنظام بدقة اكبر. تم تحضير عينات مكبوسة من النظام الثلاثي المكون من فضة، نحاس، تيتانيوم على شكل اقراص طرية. تم قياس الشدات المتألفة للنظام الثلاثي بواسطة تقنية تشتت الاطوال الموجية وفق شروط تشغيل ثابتة. تبين ان علاقة الشدة مع التركيز هي ليست خطية بسبب تأثيرات الامتصاص والتقوية ، حيث يتبين ان تأثير امتصاص الفضة للاشعة المتفلورة الناتجة عن التيتانيوم يكون اكثر من امتصاصها للاشعة المتفلورة الناتجة عن النحاس. تم استخدام معامل التأثير للنظام الثنائي من قيم الشدات النسبية لحساب تراكيز العناصر بشكل اكثر دقة باستخدام خوارزميات (بيتي - بيرسي) (BB).