DETERMINATION OF ZIRCONIUM IN BROOK SEDIMENTS BY XRF SPECTROSCOPY

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ABSTRACT.— For the determination of zirconium by X-Ray fluorescence spectroscopy in the enriched samples taken from the Sart gold research area, a new method in which rubidium is first used as an internal standard has **been** suggested. The concentrations provided by this new method in the determination of zirconium in the brook sediments and the results obtained by wet chemical analysis show (exhibit) a good conformity.

INTRODUCTION

Zirconium research works were not given the necessary importance in Turkey. Zirconium was occasionally included in some heavy mineral research studies. Recently, it has also taken place among the heavy mineral considered during the gold studies carried out in Sart area. According to this project, the determinations of zirconium and some other elements have been requested in the 47 enriched brook sediment samples taken from various parts of the area. By making use of semi-quantitative results obtained by the optical emission spectrography, the elements of these samples that are in adequate amounts for final determinations have been specified. The determinations of chromium, titanium, lanthanum and thorium elements have been made by ordinary (usual) methods.

There has not been a (particular) fixed method in the XRF spectroscopy suitable for obtaining rapid results concerning the zirconium determination in the samples that are of unusual structures and contents and also seen for the first time. By considering the facts that the interest in zirconium will increase and consequently a large amount of samples will be confronted in future, the suggestion (proposal) of a new method of analysis that will provide rapid and reliable results for zirconium determination studies by XRF spectroscopy has been appreciated.

DETERMINATION OF ZIRCONIUM IN BROOK SEDIMENTS

In the determination of zirconium by X-Ray fluorescence spectroscopy, the relation between the intensity of ZrK pig and the zirconium concentration of the sample is used (Albany, 1952). If the matrices of the samples and standards measured are not completely different, this relationship is directly proportional. But, since the analysis pig will be affected in a different way from the matrix does in the samples that have different structures and contents, the relationship may lose its proportionality which leads to (causes) wrong results of analysis. Due to the structure of the matrix, deviation from the direct proportionality may be observed as positive or negative. One of the best ways used to minimize the faults caused by the effect of matrix is the internal standard method (Adler, 1955). Although elements such as molybdenum (Brooks, 1970) and niobium (Hakkila, 1964) are used as internal standards for zirconium determination, since the brook sediments contain these elements in various proportions, it is impossible for them to be used as internal standards in the zirconium determination of the brook sediments. By the literature studies in which the criteria concerning the selection of the internal standard (Alparslan,1976) have been considered, it has been clear that rubidium can be used as internal standard element in the analysis of this type of broot sediment samples that have a different structure. It is obviously impossible for rubidium to be originally present in the brook sediments for all its compounds are soluble in water. Rubidmm provides the other necessary conditions to be used as internal standard element in the determination of zirconium. As a matter of fact, by preliminary test, it has been concluded that rubidium may be used as an appropriate internal standard element in the zirconium determination of samples taken from brook sediments of different structures.

The samples and the standards have been prepared by melting methods (Hooper, 1969). Two seperate mixtures of 1.2 % and 6.0 % RbCl concentrations have been obtained by dissolving the chlorure salt of rubidium in water, which is chosen as the internal element for zirconium, and by letting it absorb the melting substance, i.e. lithium tetraborate ($Li_2B_4O_7$). 100 mg of the sample or the appropriate standard prepared was added to the 1000 mg part taken from one of these mixtures and they have been melted in 1100°C for 20 minutes. The beads formed by cooling were increased to 1500 mg by the addition of binder cellulose and they have been ground less than 200 mesh and molded as tablets by pressing. As standards were being prepared, a mixture sythesized by making use of semi-quantitative results obtained by the optical emission specktra of the samples was used. In certain amounts fine-powdered ZrO_2 (spex) was added to this mixture which has a similar matrix to that of the samples, and a series of standards, concentrations known, have been obtained.

The measurements of the standards and the tablet shaped samples were made by the SPC-S vacuum spectrometer of the General Electric Company. The working conditions are given in Table 1.

Table 1 - The measurement conditions in which rubidium is used as internal standard element for zirconium determination in the brook sediment samples

Crystal	: Fibril
Anticathode	: W
Tube tension	: 50 KV
Tube flux intensity	: 40 mA
Crack width	: 1.27 mm
Duration of measurement	: 20 seconds
Pressure	: Vacuum
Tension of counter	: 1240 V
Space between windows	: 2-6 V
Angles (2θ)	: $ZrK\alpha = 31°.55$
	$RbK\alpha = 37°.40$
	$RbK\beta = 33°.20$

As internal standard pigs that may be added to ZrK_a (20 = 31°.55) which has been selected as analysis pig, RbK_a(20 = 37°.40) in 1.2 % RbCl concentrated samples and standards and RbK_b (20 = 33°.20) pig in 6.0 % RbCl concentrated samples and standards have been measured. By the evaluation of the measurement results, the pig intensity ratios of $IZrK_a$ / $IRbK_a$ and $IZrK_a$ / $IRbK_b$ have been formed. By making seperate graphs of these proportions against the zirconium concentrations of the standards, two working curves have been obtained.

The spectra of 6.0 % RbCl concentrated standard when RbK$_b$ pig is measured as internal standard are shown in Figure 1. Although the ZrK$_a$ and RbK$_b$ pigs are to each other within the seperative limits of the spectrometer, they do not affect one another in the concentration interval designated in Figure 1. By preparing graphs of IZrK$_a$ / IRbK$_b$ intensity ratios taken from this spectrum and the zirconium concentrations of the standards, a working curve, correlation coefficient 0.999, has been obtained (Fig. 2). But, as the zirconium concentration increases, ZrK$_a$ pig gets larger in equal proportion and affects the RbK$_b$ pig. As a result of this, RbK$_b$ pig seems to be larger than it is and the IZrK$_a$ / IRbK$_b$ intensity ratio decreases. And this results in a negative deviation in the highly concentrated part of the working curve. The working curve, seen as a straight line up to 1.5 % ZrO$_2$ concentration, bends towards the horizontal axis in the concentrations above the boundary (limit). The RbK$_a$ pig which is considered to give better results for the concentrations above this limit takes place in the spectrum some distance from the ZrK$_b$ pig that enables it not to be affected by all the concentrations. The spectra of 1.2 % RbCl concentrated standards in which RbK$_a$ pig is taken as internal standard are shown in Figure 3. The working curve obtained by the preparation of the graph of IzrK$_a$ /IRbK$_a$ pig intensity ratio taken from this spectrum against the ZrO concentrations of more than 1.5 % is a straight line and the correlation coefficient is 0.996 (Fig. 4). As it is seen, in the part bearing high zirconium concentrates in which negative deviations are observed in the pig intensity ratio IZrK$_a$ / lRbK$_a$, the working curve has been formed as a straight line without any deviations, the intensity ratio IZrK$_a$ / IRbK$_b$ has been used.

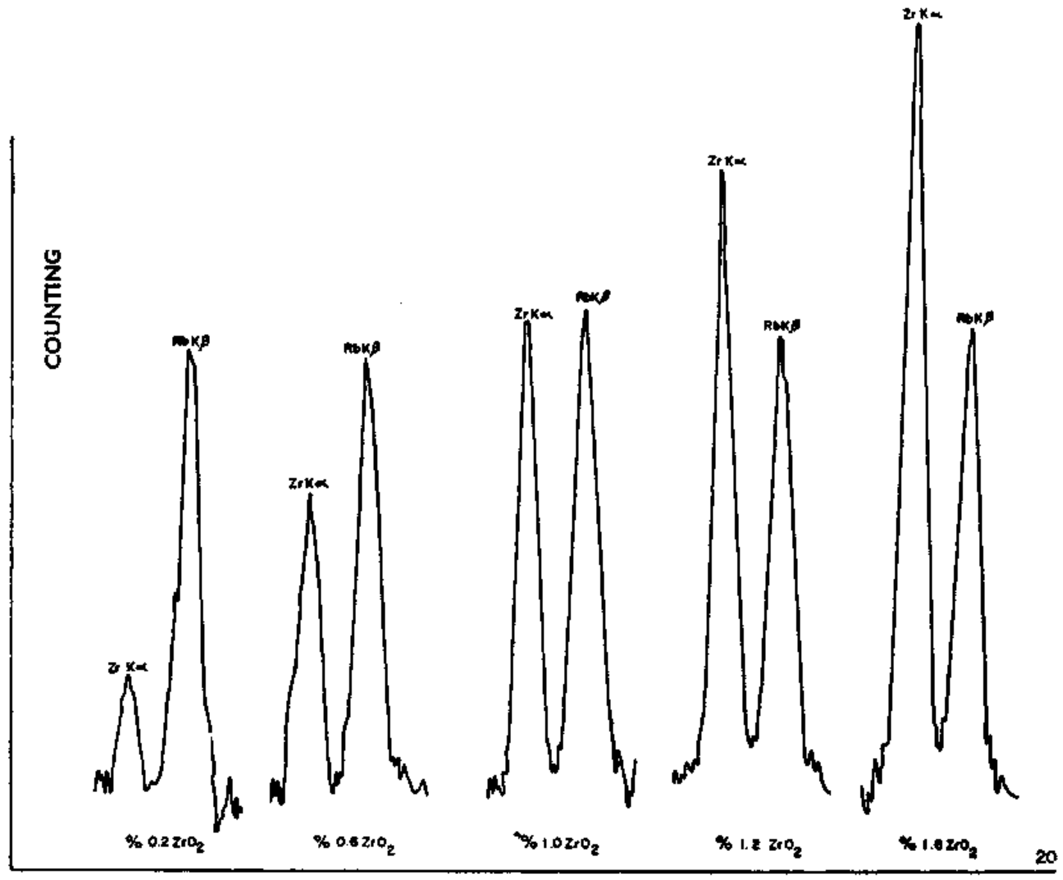

Fig. - 1

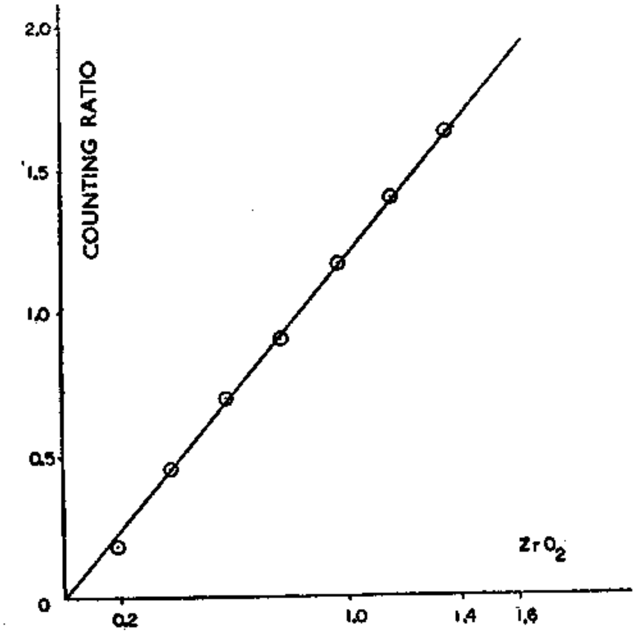
2,0
1,5
1,0
0,5
0
COUNTING RATIO
Zr O$_2$
0,2
1,0
1,4
1,6

Fig. 2 -

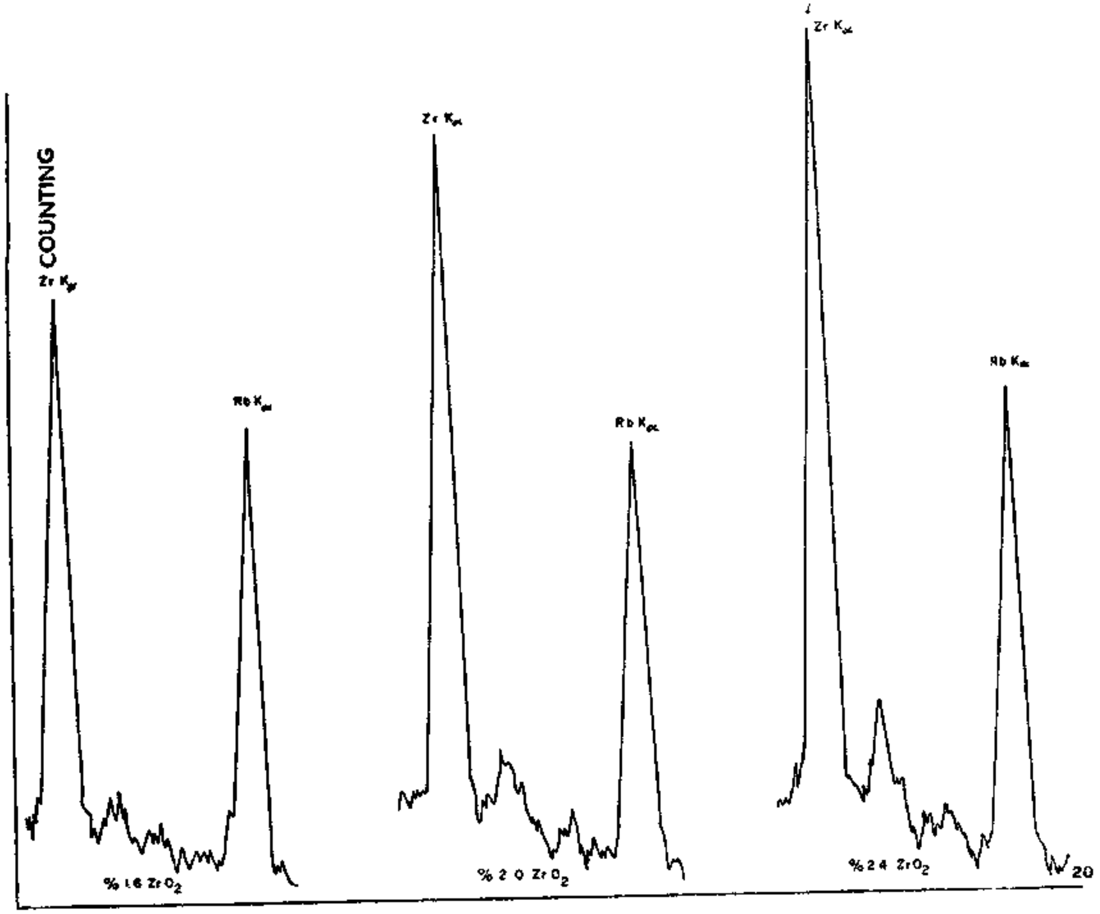
COUNTING
Zr Kα
Rb Kα
Zr Kα
Rb Kα
Zr Kα
Rb Kα
% 1.6 Zr O$_2$
% 2.0 Zr O$_2$
% 2.4 Zr O$_2$
20

Fig. 3 -

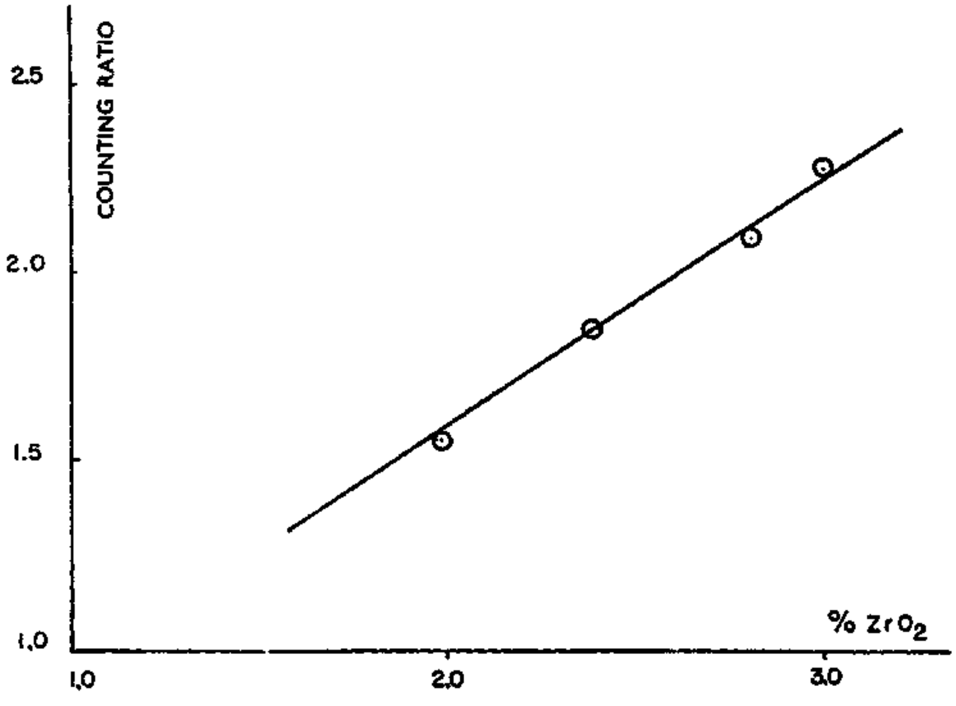

Fig. 4 -

RESULTS

The zirconium concentrates of the samples have been determined by making use of one of the working curves according to their zirconium contents and pig intensity ratios obtained by measurements. Results obtained by this method display a great difference from the values obtained by measurements in which no internal standards have been used. The values provided by wet chemical analysis of 5 brook sediment samples containing different amounts of zirconium, show a better conformity with the zirconium concentrates obtained by the new method in which rubidium has been as the internal standard. Table 2. shows merely the analysis results of 5 brook sediment samples of which chemical analyses are completed.

Table 2 - The zirconium concentrates of 5 brook sediment samples provided by XRF, chemical analyses done (as ZrO_2 %)

Sample no.	*Without internal standard*	*With internal standard*	*Chemical analysis*
1	2.66	3.06	3.00
2	0.95	1.20	1.28
3	1.88	2.18	2.16
4	0.78	0.90	1.00
5	0.27	0.39	0.45

In this method, the corruptive elements that may influence the zirconium analysis results may be U, Pb, Bi, Pt, Au, Te, Y, Hf. But, according to the results obtained by the semi-quantitative results of the optical emission spectrograph of the brook sediment samples analized, none of these elements is of enough amount to affect the analysis pigs. A new analysis method which provides rapid and reliable results easily applicable to samples of different structures and contents such as brook sediments and in which rubidium is for the first time used as internal standard for low and high zirconium concentrates, has been suggested in the present article.

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