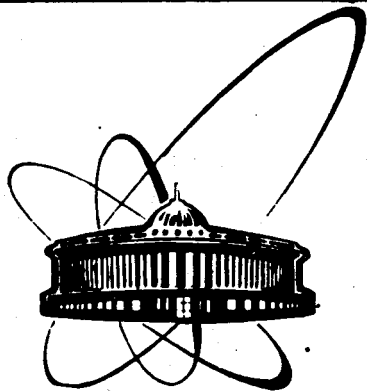


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ОБЪЕДИНЕННЫЙ  
ИНСТИТУТ  
ЯДЕРНЫХ  
ИССЛЕДОВАНИЙ  
ДУБНА

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E14-89-493

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APPLICATION OF THE EMPIRICAL MATRIX  
EFFECT CORRECTION METHODS  
IN PIXE ANALYSIS OF Y-Ba-Cu-O CERAMICS

Submitted to XXVI Colloquium Spectroscopicum  
Internationale, Sofia

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1989

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E14-89-493

Применение методов эмпирических коэффициентов  
в решении матричных эффектов при PIXE анализе  
Y-Ba-Cu-O керамик

Приводится методика анализа высокотемпературных сверхпроводников, основанная на поправке матричных эффектов методами эмпирических коэффициентов. Методика разработана на эталонных смесях, составленных из порошков  $\text{CuO}$ ,  $\text{Y}_2\text{O}_3$  и  $\text{BaCO}_3$ . Были изучены выбранные эмпирические методы коррекции матричных эффектов спектрометрии ХРИ с поправкой на концентрацию, а также на интенсивность. Хорошие результаты получены с помощью модели Мишель-Хопфера, где правильность определения для Y, Ba и Cu не была хуже чем 3,3 относительных % для иттрия и 1,0 отн. % для бария и меди. Точность анализа может быть достигнута на уровне около 1%.

Работа выполнена в Лаборатории нейтронной физики ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1989

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E14-89-493

Application of the Empirical Matrix Effect  
Correction Methods in PIXE Analysis  
of Y-Ba-Cu-O Ceramics

The simple technique for PIXE analysis of high temperature superconducting materials based on the empirical matrix effects correction methods is presented. The technique has been developed using the reference materials composed of the known content of powders of  $\text{CuO}$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{BaCO}_3$ . The chosen empirical methods of x-ray spectrometry based both on concentration correction and on intensity correction have been tested. The best results have been obtained applying the Mitchell and Hopper model, in this case the accuracy of the determination of Y, Ba, and Cu was not less than 3.3 relative % for yttrium and 1.0 relative % for barium and copper respectively. The precision of the analysis can be obtained by approximately 1%.

The investigation has been performed at the Laboratory of Neutron Physics, JINR.

Preprint of the Joint Institute for Nuclear Research. Dubna 1989

## INTRODUCTION

The development and study of high temperature superconducting ceramics call for nondestructive analytical techniques promising sufficient precision and accuracy of the determination. The particle induced x-ray emission (PIXE) method is suitable to be applied in analysis of bulk samples as well as thin solid films of this kind of materials<sup>1,2</sup>. On the other hand, the achieved accuracy of the Y, Ba as well as Cu determination (4-5 relative %) is not very sufficient to solve a number of technological or physical problems. It is known that in x-ray fluorescence analytical techniques the precision of analysis depends on matrix effects in analysed system, kind of physical or interelement character. With the aim to achieve higher accuracy of PIXE analysis of high- $T_c$  superconductors composed of Y, Ba, Cu, and O the application of methods of matrix effects correction have been incorporated in the calculation algorithm. At present there are many of the empirical methods of interelement effects correction in x-ray spectroscopy based on both the correction on concentration<sup>3,4</sup> and intensity<sup>5,6</sup>. The aim of the present work has been to find optimal correction model for PIXE analysis of high- $T_c$  superconducting materials composed of Y-Ba-Cu-O.

## EXPERIMENTAL

For the external standards the reference samples, prepared from pure powders of CuO, BaO, and BaCO<sub>3</sub>, have been

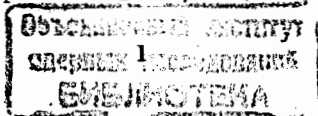


Table 1. The certified values of concentration for 12 reference samples and corresponding x-ray yields measured under activation with 3.0 Mev <sup>4</sup>He ions

N	element	C (g/g)	Yield	N	element	C (g/g)	Yield
1	O	0.1693	-	7	O	0.1602	-
	Cu	0.2988	125 191		Cu	0.2914	127 122
	Y	0.2090	146 816		Y	0.1495	100 593
	Ba	0.3229	1 329		Ba	0.3989	1 587
2	O	0.1552	-	8	O	0.1624	-
	Cu	0.2569	103 181		Cu	0.2932	126 162
	Y	0.1438	97 766		Y	0.1641	105 022
	Ba	0.4441	1 880		Ba	0.3803	1 418
3	O	0.1626	-	9	O	0.1647	-
	Cu	0.3445	148 401		Cu	0.2951	125 490
	Y	0.1205	90 806		Y	0.1789	124 120
	Ba	0.3724	1 722		Ba	0.3613	1 386
4	O	0.1515	-	10	O	0.1716	-
	Cu	0.2834	118 610		Cu	0.3005	123 614
	Y	0.0930	65 951		Y	0.2248	164 143
	Ba	0.4721	2 088		Ba	0.3031	1 053
5	O	0.1537	-	11	O	0.1495	-
	Cu	0.2863	131 315		Cu	0.2827	125 556
	Y	0.1067	74 667		Y	0.0791	54 167
	Ba	0.4534	1 956		Ba	0.4887	2 087
6	O	0.1558	-	12	O	0.1670	-
	Cu	0.2879	126 442		Cu	0.2969	119 027
	Y	0.1208	87 343		Y	0.1939	115 687
	Ba	0.4355	1 969		Ba	0.3422	1 481

used. After mixing the aliquots have been pressed into the pellets. The composition of all samples is given in table 1.

For the irradiation of the samples the 3.0 Mev <sup>4</sup>He ions of the van de Graaff accelerator in JINR have been used. The yields of K<sub>α</sub> lines of Cu(8.9 keV), Y(14.6 keV), and Ba(32.6 keV) have been chosen for quantitative determination of Cu, Y, and Ba (see table 1). The more detailed description of experimental conditions has been already published<sup>1</sup>.

#### CALCULATIONS

To solve (C<sub>i</sub> - Y<sub>i</sub>) concentration - x-ray yield relation in analysed system, in analytical practice linear or quadratic relations are often used. According to the interval as well as to the variation of the concentration in all samples, the discussed expressions cannot always describe the analysed system sufficiently. Allowance for additional empirical coefficients describing interelement effects can lead to improving the accuracy of the analysis. The following models have been tested in our Y-Ba-Cu-O system:

$$C_i = a + b Y_i \quad (1)$$

$$C_i = R_i \left( 1 + \sum_{j \neq i} \alpha_{ij} C_j \right) \quad (2)$$

proposed by Lachance and Traill<sup>3</sup> (L-T),

$$C_i = R_i \left( 1 + \sum_{j \neq i} \alpha_{ij} C_j + \sum_{j \neq i} \beta_{ij} C_j / (1 + C_i) \right) \quad (3)$$

proposed by Rasberry and Heinrich<sup>4</sup> (R-H),

$$C_i = R_i \left( 1 + \sum_{j \neq i} k_{ij} R_j \right) \quad (4)$$

proposed by Lucas-Tooth and Pierce<sup>5</sup> (LT-P),

$$C_i = 1 + \sum_j k_{ij} R_j + \sum_j \sum_{k \neq j} k_{ijk} R_j R_k \quad (5)$$

$$C_i = k_o + \sum_j k_{ij} R_j + \sum_j k_{ijj} R_j^2 + \sum_j \sum_{k \neq j} k_{ijk} R_j R_k \quad (6)$$

proposed by Mitchell and Hopper<sup>6</sup> (M-H).

In equations (2)-(6)  $\alpha_{ij}$ ,  $\beta_{ij}$  and  $k_{ij}$ ,  $k_{ijj}$ ,  $k_{ijk}$  are empirical coefficients expressing the influence of a j-th element on the i-th one (or j-th and k-th on the i-th one in the M-H model),  $R_i$ ,  $R_j$ ,  $R_k$  are the relative yields of x-ray radiation for the i-th, j-th and k-th element, respectively, and  $C_i$ ,  $C_j$  are the relative concentrations.

The calculation of empirical coefficients from equations (2) - (6) has been performed on reference samples using the program FUMILI<sup>8</sup> handling data by the method of least squares in the general method of maximum likelihood. Applying calculated coefficients and experimental x-ray yields of  $K_{\alpha}$  lines the concentrations  $C_i^{calc}$  of Y, Ba, and Cu have been determined. In this step the certificated concentration of oxygen has been taken into account. With the aim to compare the accuracy of the applied techniques the residual dispersion  $s$  has been used, defined in the following way:

$$s = \frac{\sum_i (C_i^{calc} - C_i^{true})^2}{N - p},$$

where  $C_i^{true}$  is true concentration,  $C_i^{calc}$  is calculated

concentration,  $N$  is number of the standards and  $p$  express the number of empirical parameters.

The values of  $s$  for all tested correction models as well as linear relation (1) are given in table 2. The best results have been obtained using the Mitchell - Hopper empirical relation, where the accuracy of determination is not worse than 3.3 relative % for yttrium and 1.0 relative % for barium and 0.9 for copper. The dependence of  $C^{calc}$  on  $C^{true}$  for Y, Ba and Cu applying the M-H model are given in figures 1, 2 and 3 respectively. The illustrated best fit in the figures is complemented by the results obtained without interelement effects correction to demonstrate the advantage of the proposed technique.

Table 2. Calculated residual dispersion  $s$  for the determination of Y, Ba and Cu by the chosen empirical models

Model Number	residual dispersion		
	Y	Ba	Cu
1	$1.4 \cdot 10^{-2}$	$1.7 \cdot 10^{-2}$	$1.0 \cdot 10^{-2}$
2	$0.7 \cdot 10^{-2}$	$1.6 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$
3	$0.6 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$	$1.1 \cdot 10^{-2}$
4	$0.9 \cdot 10^{-2}$	$1.6 \cdot 10^{-2}$	$0.9 \cdot 10^{-2}$
5	$2.7 \cdot 10^{-2}$	$1.8 \cdot 10^{-2}$	$1.1 \cdot 10^{-2}$
6	$0.5 \cdot 10^{-2}$	$0.3 \cdot 10^{-2}$	$0.2 \cdot 10^{-2}$

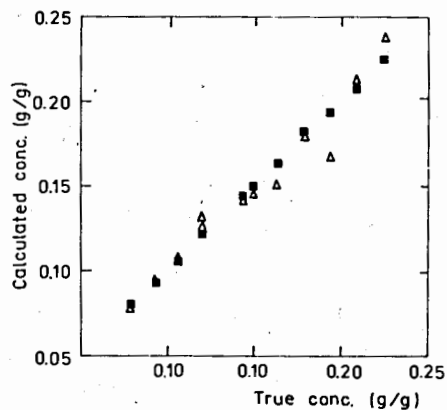


Fig. 1. The dependence of  $C^{calc}$  on  $C^{true}$  for yttrium,  
 ■ using the Mitchell-Hopper interelement correction model  
 △ without interelement correction technique

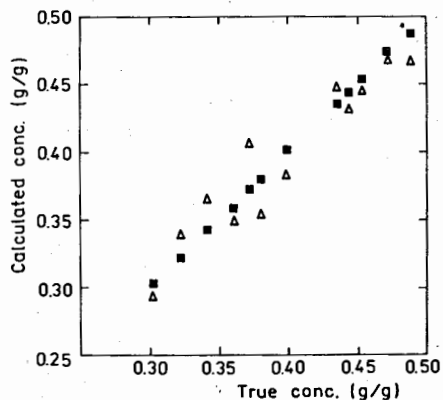


Fig. 2. The dependence of  $C^{calc}$  on  $C^{true}$  for barium,  
 ■ using the Mitchell-Hopper interelement correction model  
 △ without interelement correction technique

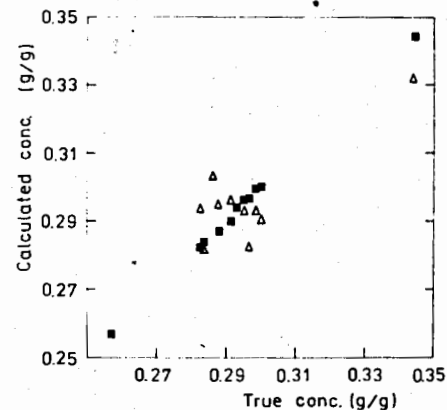


Fig. 3. The dependence of  $C^{calc}$  on  $C^{true}$  for copper,  
 ■ using the Mitchell-Hopper interelement correction model  
 △ without interelement correction technique

It can be seen from the figures that in the PIXE analysis of high- $T_c$  superconducting materials, application of the interelement effect correction can give sufficient accuracy. The preparation of good reference samples, not degrading with time, is still the main question in proposed technique.

#### ACKNOWLEDGEMENTS

I would like to thank to Dr.D.Valentovic for preparation of standard samples and thanks are due to Dr.A.P.Kobzev for valuable discussions and interest in this work. Also I am indebted to the whole Van de Graaff accelerator staff for their devotion in running the accelerator.

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Received by Publishing Department  
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