

Development of the Titrimetric and Spectrophotometric Methods for Determination of the Oxygen Content in Superconducting Cuprates

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Authors' contributions

This work was carried out in collaboration between all authors. Author SG designed the study, performed the analysis, wrote the protocol and wrote the first draft of the manuscript. Authors SG, TN and ASI managed the analyses of the study. Author SG managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

This review article is concerned with the oxygen stoichiometry determination in $\text{YBa}_2\text{Cu}_3\text{O}_y$ and $\text{REBa}_2\text{Cu}_3\text{O}_y$ (RE = Er, Eu, Gd) superconductors. The nondestructive and destructive methods for the determination of the oxygen coefficient y ($y = 6.5 + \delta$, δ is the non-stoichiometric oxygen coefficient) are described. The destructive methods as titrimetry and spectrophotometry are discussed in detail. The role of the reducing agent for Cu(III) ions from the superconductor sample is clarified. A number of new formulae for calculation δ - and y - coefficients of the oxygen are reviewed.

The advantages and disadvantages of the iodometric titrations and the spectrophotometric methods are given. Spectrophotometric methods without calibration of the analytical function and/or using small sample mass for analysis are preferable because: analysis with them is not expensive; the results are accurate; they can be applied to determine the oxygen stoichiometry of the

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superconducting thin film deposit into substrates. One of them has been developed and employed for the first time to determine the oxygen stoichiometry in Ca doped REBa₂Cu₃O_y high-T_c bulk materials.

Keywords: Oxygen determination; Cuprates; YBCO; Superconducting materials; titrimetry; spectrophotometry.

1. INTRODUCTION

The finding of the ceramic superconducting materials in the end of 1986 posed a lot of new issues in the development of modern science and technologies [1-10]. During the past years the superconducting materials have been increasingly making their way into various spheres of industry, transport and engineering (medical equipment, chemical industry, microelectronics etc.), as well as into new technologies for astronautic and military purposes [11]. Getting of and studying the properties of the superconducting materials caused very deep interest amongst the scientists from all over the world. Some national programs were created in many countries related to large-scale financing. The interest towards superconducting materials is due to their primary property – lack of any electric resistance under low temperatures [12-14]. The conductance of electricity through them is carried out with no loss of energy in the form of heat, which shall lead to decreasing the electric charge of electric power produced and of harmful emissions released such as CO₂ etc. The great interest to them has been kept up to the present due to the exceptional prospects of changing the development of human civilization by introducing of the superconducting materials in the way of life and engineering.

During the past years the activity on synthesizing and investigating of superconducting materials (volumetric specimens, thin films, silver-coated test specimens, and high-temperature superconducting tapes) has been kept, aiming at their practical application.

Amongst the superconducting systems known by now the largest number of publications has been dedicated to the system Y-Ba-Cu-O (YBCO) – YBa₂Cu₃O_y phase, [15,16]. High-temperature superconductivity with T_c = 70÷98 K has been observed also in a whole row of ceramic materials, derivative of YBCO, with the general formula of REBa₂Cu₃O_y (REBCO), where RE is a rare-earth element and y = 6.5+δ, as well as in materials in which part of RE has been

substituted with calcium. “δ” shall stand for the non-stoichiometric, also called active oxygen. The value of δ varies within 0 ≤ δ ≤ 0.5. The rising up of δ leads to sharp change to the critical temperature (T_c) as well as to change of the materials’ structure from tetragonal to orthorhombic [12-29]. One of the issues still pending for solution in parallel with the technology of the ceramic materials is the analytical control of the oxygen content. The oxygen content acts as a regulating factor of the structure and the electrical properties of YBCO superconducting materials and that is why its control has to be done.

The reasons for the higher value of the oxygen coefficient than the stoichiometric one (y = 6.5) are not clarified. The nature of the oxidation of superconducting cuprates has also not been established. Some authors explain the higher value of the oxygen coefficient with variable valency of the metal atoms of the elements Cu, Bi, Tl, and Pb (Cu(III)/Cu(II), Bi(V)/Bi(III), Tl(III)/Tl(I) and Pb(IV)/Pb(II)) in the structure of the superconducting material [17-23]. Other researchers [24] explain the presence of active oxygen with the capability of the cupreous atoms to exist in (II) and (III) degrees of oxidation in the structure of the superconducting material by intermodal interaction $2\text{Cu}^{2+} - 2\text{O}^{2-} \leftrightarrow 2\text{Cu}^{3+} + \text{O}_2$, which creates oxygen vacancy in the crystal lattice.

Rao and all [25] associate the presence of an active oxygen in YBCO superconductors with "holes" in the crystal lattice. There are suggestions that these "holes" are mobile, located in the electronic bands [26].

Other authors show that the electroneutrality of the YBa₂Cu₃O_y (y > 6.5) molecule is due to the variable oxygen degree of oxidation as an atomized oxygen, oxygen (-1) degree of oxidation in the complex [CuO]⁺ or a peroxide oxygen O₂²⁻ [27].

The dependence between the oxygen content and the superconducting properties of the

superconducting materials makes the oxygen content determination necessary. Therefore methods for its determination should be developed. By now, the non destructive and destructive methods for the oxygen determination are known in literature.

Many non destructive methods like X-ray diffraction [18,29], photoelectron and Auger spectroscopy, Raman spectrometry [30-33] and electron microanalysis have been developed for the determination of the oxygen coefficient "y" in RE₁Ba₂Cu₃O_y materials if appropriate mathematical relations "oxygen content–physical parameter" are preliminary found. For example, powder XRD-spectrometry gives the monophasic of YBCO samples and determines the oxygen coefficient y [18]. The "y" value is calculated by the equation $y = 75.250 - 5.856 c$ [18], where "c" is unit cell parameter of YBa₂Cu₃O_y. The accuracy and precision of parameter "c" as well the "y" coefficient is not as good as the accuracy and precision of "y" determined by destructive methods.

The destructive methods (methods for analysis of average sample) are: thermogravimetric methods [34,35], gas volumetric methods [15,35], Voltamperometry with hard superconducting electrode [36] and methods with pre-dissolving of the sample ("Wet methods") [15,24,37-64]: iodometric titration [29-47] spectrophotometric [13,17,56-63] and coulometric [64-66] methods.

It should be noted that thermogravimetry and gas volumetric analysis determines the total oxygen ratio (y) while the "wet method" determines the non-stoichiometric oxygen coefficient δ .

2. WET METHODS

The spectrophotometric and titrimetric methods are used more than the coulometric methods. The reason for that is obtaining analysis information with high degree of reliability without using expensive equipment for analysis. The solvent in the spectrophotometric and titrimetric methods often is hydrochloric acid [19,42,45-49,51-72], but the sample may be also dissolved in hydrobromic acid [50,65], phosphoric acid [49], acetic acid or acetate buffer solution (pH ~4.5). Dissolution is carried out in the presence of iodide ions [56-60,70], bromide ions [68], Co (II) [71], Fe (II) [28,69], or other reductant.

In order to calculate the non-stoichiometric oxygen coefficient δ the hypothesis of existence

of copper (II) and copper (III) degree of oxidation has been accepted. Therefore the chemical formula of REBCO is written in the form

$\text{REBa}_2\text{Cu}_{3-z}^{2+}\text{Cu}_z^{3+}\text{O}_{6.5+z/2}$ where $\frac{z}{2} = \delta$ and the

coefficient δ is calculated as follows:

A. The quantities of Cu(III) and total copper are calculated owing to the ratio

$$\frac{n_{\text{Cu(III)}}}{n_{\text{Cu(II)}} + n_{\text{Cu(III)}}} = \frac{z}{3} \text{ and the oxygen coefficient}$$

δ is obtained as a result of the equation:

$$\delta = 1.5 \frac{n_{\text{Cu(III)}}}{n_{\text{Cu(II)}} + n_{\text{Cu(III)}}} \quad (1)$$

B. The oxygen coefficient δ is also calculated by the equation:

$$\delta = \frac{z}{2} = \frac{M_{\text{REBCO}} n_{\text{Cu(III)}}}{2m - M_{\text{O}} n_{\text{Cu(III)}}} \quad (2)$$

Where M_{REBCO} и M_{O} are the molar masses (g mmol^{-1}) of $\text{REBa}_2\text{Cu}_3\text{O}_{6.5}$ (RE=Y, La, Sm, Ho, Lu, Eu, Er, Gd, Dy) and the oxygen atom, respectively, "m" is the sample mass (g) and "n" are the mmols of Cu(III).

The results for the δ coefficient founding by the two approaches coincide when the model is a single-phase [48]. Mismatch is indirect evidence for the existence of other phases except phase $\text{REBa}_2\text{Cu}_3\text{O}_{6.5} + \delta$. When the samples are analysed with unproven homogeneity, analytical results are usually presented as % Cu(III) or as a ratio of Cu(III) and the total copper.

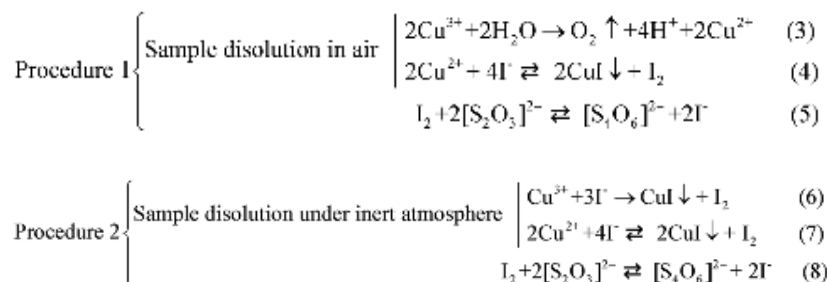
2.1 Iodometric Titrimetric Methods

Classical for the analysis of the oxygen content are the iodometric titrimetric methods, based upon the reduction properties of the iodide ions against Cu(II) and Cu(III) (the content of Cu(III) corresponds to the active oxygen). The analysis is conducted by dissolving and titration of two individual samples, or by two consecutive titrations of only one sample.

2.2 Analysis by Dissolution and Titration of Two Individual Samples

The determination of active oxygen by dissolving and titration of two individual samples [38-40]

includes: 1) dissolving of the sample in a hydrochloride acid medium (from 0.1 to 2 mol l⁻¹) and classical iodometric determination of the total copper (Procedure 1, Eqs. 3, 4 and 5); 2) dissolving the sample in a hydrochloride medium under an inert atmosphere in the presence of potassium iodide and titration of the iodine released in reactions 6 and 7 (Procedure 2).



According to Nazzal et al. [37] in Procedure 1 the reduction of Cu (III) to Cu (II) proceeds as follows: $2[\text{CuO}]^+ + 2\text{H}^+ \rightarrow 2\text{Cu}^{2+} + \text{H}_2\text{O} + 0.5\text{O}_2$ and in Procedure 2 – Reaction 6 is replaced by the reaction $[\text{CuO}]^+ + 3\text{I}^- + 2\text{H}^+ \rightarrow \text{CuI} \downarrow + \text{I}_2 + \text{H}_2\text{O}$.

The amount of Na₂S₂O₃ in Procedure 1 (Eq.5) is $n_1 = n_{\text{Cu(III)}} + n_{\text{Cu(II)}}$ while the quantity of thiosulphate in Eq. 8 (Procedure 2) is $n_2 = n_{\text{Cu(II)}} + 2n_{\text{Cu(III)}}$. The results in the amount of Na₂S₂O₃ by both procedures are brought to the same sample mass and Eq. 1 takes the following form:

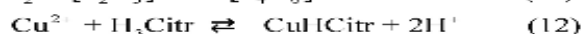
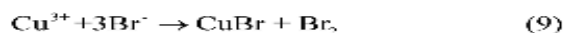
$\delta = 1.5 \frac{n_2 - n_1}{n_1} = 1.5 \frac{(V_2^{\text{eq}} - V_1^{\text{eq}})}{V_1^{\text{eq}}}$, where V_1^{eq} and V_2^{eq} are the equivalent volumes of Na₂S₂O₃ from the first and second procedure.

According to other authors [41] the amount of Cu(III) in Procedure 2 can be found by dissolving the sample in presence of Fe (II) and back dichromate titration of the amount of Fe(II). The quantities of copper from the both procedures are brought to the same sample mass and it is replaced in Eq. 1:

$\delta = \frac{n_{\text{Cu(III)}}}{n_{\text{Cu}}}$, where $n_{\text{Cu(III)}}$ is determined by dichromate titration, and the total copper n_{Cu} – by

iodometric titration (Procedure 1). However this method has the same disadvantages as the method for dissolving two individual samples as well as applying two different titrimetric methods.

The iodometric method with sample dissolving in 4,4 mol.l⁻¹ solution of hydrobromic acid at low temperature has been also known [42]. After that KI is added and the titration with thiosulphate is performed in the presense of citric acid (H₃Citr). The reactions of the method are:



The non-stoichiometric oxygen coefficient is calculated by Eq. 2 where the amount of Cu(III) is expressed as the quantity of thiosulphate: $n_{\text{Cu(III)}} = n_{\text{I}_2} = \frac{1}{2} n_{\text{Na}_2\text{S}_2\text{O}_3}$

Disadvantages of the above method are: (1) necessity of maintaining a narrow range of the temperature and acidity of the medium and (2) separation of toxic bromine during analysis.

The results of the discussed classical iodometric methods often give errors due to the following processes:

- Oxidation of the iodide ions from the air oxygen during the titration. [69] The process is highly influenced by the presence of multivalent copper ions and the acidic medium of titration.
- Adsorption of iodine on the copper iodide precipitate.

Y. Maeno et al. [44] offer the two individual titrations to be held in an acetate medium with a $\text{pH} \approx 3$ in order to minimize the oxidation of the iodide ions from the air oxygen. To eliminate the adsorption of iodine on the precipitate of copper iodide an amount of potassium thiocyanate has been added to the solution [46].

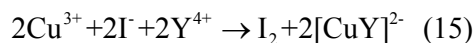
2.3 Analysis by Two Consecutive Titrations of One Sample

An improvement of the iodometric methods requiring dissolving two samples is achieved by two consecutive iodometric titrations of only one sample.

The sample has been dissolved in hydrochloric acid solution of potassium iodide under an inert atmosphere [47]. Reactions take place as follows:



Sodium acetate-acetic acid buffer ($\text{pH} 4.8$) and EDTA (H_4Y) are added to the sample solution. $\text{Cu}(\text{II})$ and EDTA ions form a complex and the equilibrium of reaction 14 is pulled to the left. Products obtained by reaction 13 react also by Eq. 14 giving Cu^{2+} -EDTA complex. Thus the reaction of $\text{Cu}(\text{III})$ can be given by the equation:



The iodine liberated by Eq. 15 is equivalent to the amount of $\text{Cu}(\text{III})$: $n_{\text{I}_2} = \frac{1}{2} n_{\text{Cu}(\text{III})}$. It is titrated with standard thiosulfate solution by Eq. 11. After first titration a strong inorganic acid and

an additional amount of potassium iodide are added to the solution and the complex of $\text{Cu}(\text{II})$ with EDTA is destructed. A quantity of I_2 equivalent to the total amount of copper

$n_{\text{I}_2} = \frac{1}{2} (n_{\text{Cu}(\text{III})} + n_{\text{Cu}(\text{II})})$ is liberated and titrated with a solution of $\text{Na}_2\text{S}_2\text{O}_3$. The equivalent point of both titrations is established visually with starch solution. Later, the visual indication was replaced with instrumental [48].

The y coefficient could be calculated by Eq. 16 or by Eq. 17. However in the second equation the sample mass and the concentration of thiosulphate must be known.

$$y = 6.5 + 1.5 \frac{n_{\text{Cu}(\text{III})}}{n_{\text{Cu}}} = 6.5 + 1.5 \frac{V_1}{V_2} \quad (16)$$

$$y = 6.5 + \frac{M_{\text{YBCO}} C_{\text{st}} V_1}{2m - A_{\text{O}} C_{\text{st}} V_1} \quad (17)$$

V_1 and V_2 are the volumes (in ml) of the solution of sodium thiosulfate consumed in the first and second titration; M_{YBCO} and A_{O} are the molecular and atomic masses (g mmol^{-1}) of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ sample and the oxygen, respectively; C_{st} is the concentration (mol l^{-1}) of sodium thiosulfate and m - sample mass (g).

The titrimetric methods for determination of the oxygen stoichiometry of YBCO samples, using iodide ions as reducing agent are summarized in Table 1.

The mass of the sample used for analysis in all titrimetric methods is about 100 mg. This not so low mass of the sample leads to titration of high concentrations of iodine, which is connected with loss of iodine as a result of its volatility and oxidation of the iodide ions by the oxygen in the air. These are the disadvantages of all the iodometric titrimetric methods.

2.4 Spectrophotometric Methods

During the past few years the superconducting materials have been used in electronics in the form of thin films upon substrates, in which the mass of the superconducting material is too low (less than 1mg) and the analytical control of the oxygen content may not be carried out by already known methods. This is why many authors have been investigated the spectrophotometry for determining the oxygen content.

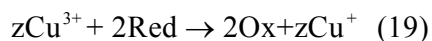
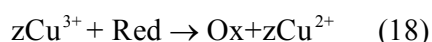
Table 1. Iodometric methods for determination of oxygen stoichiometry of YBCO bulk samples; $m_{\text{sample}} = 100 \text{ mg}$

Sample dissolving	Measurement of the analytical signal	Mole ratios of the reactions of dissolution and titration	Formula for calculation of δ
Two samples in a hydrochloride medium: (Procedure 1) under atmospheric conditions, and (Procedure 2) under inert atmosphere in the presence of KI [38-40].	<p><i>Procedure 1.</i> Iodometric titration of the total copper</p> <p><i>Procedure 2.</i> Titration of iodine, equivalent to the sum: $n_{\text{Cu(II)}} + 2n_{\text{Cu(III)}}$.</p>	<p><i>Procedure 1</i></p> $n_{\text{I}_2} = \frac{1}{2}(n_{\text{Cu(III)}} + n_{\text{Cu(II)}});$ $n_{\text{Na}_2\text{S}_2\text{O}_3} = n_{\text{I}_2}$ <p><i>Procedure 2</i></p> $n_{\text{I}_2} = \frac{1}{2}n_{\text{Cu(II)}} + n_{\text{Cu(III)}};$ $n_{\text{Na}_2\text{S}_2\text{O}_3} = n_{\text{I}_2}$	$\delta = 1.5 \frac{V_2^{\text{eq}} - V_1^{\text{eq}}}{V_1^{\text{eq}}}$
A sample in a hydrochloride medium under an inert atmosphere in the presence of KI [47].	<p>Two successive titrations of I_2 with a solution of $\text{Na}_2\text{S}_2\text{O}_3$.</p> <p><i>Titration 1.</i> Acetate medium (pH 4.8) in the presence of EDTA.</p> <p><i>Titration 2.</i> Hydrochloride acid medium after adding of extra H_2SO_4 and KI.</p>	<p><i>Titration 1</i></p> $n_{\text{I}_2} = \frac{1}{2}n_{\text{Cu(III)}}; n_{\text{Na}_2\text{S}_2\text{O}_3} = n_{\text{Cu(III)}}$ <p><i>Titration 2</i></p> $n_{\text{I}_2} = \frac{1}{2}(n_{\text{Cu(III)}} + n_{\text{Cu(II)}});$ $n_{\text{Na}_2\text{S}_2\text{O}_3} = 2n_{\text{I}_2}$	$\delta = 1.5 \frac{V_1}{V_2}$ <p>or</p> $\delta = \frac{M_{\text{YBCO}} C_{\text{st}} V_1}{2m - M_{\text{O}} C_{\text{st}} V_1}$

The spectrophotometric methods for analytical control of the oxygen content of REBCO superconductive materials can be divided into two groups: Methods with calibration and methods without calibration of the analytical function.

2.5 Methods with Calibration of the Analytical Function

In these methods the sample is dissolved under inert atmosphere in the presence of a reducing agent (Red). One of the following oxidation reactions proceeds:



The oxidizing agent (Ox) or unreacted reducing agent (Red) absorbs UV / Vis radiation. The absorbance of the solution is measured and the concentration of liberated oxidizer/unreacted reducer is calculated by Beer's law after previous calibration of the analytical function. The non-stoichiometric coefficient δ is calculated by Eq. 2 where the amount of Cu(III) is replaced with the equivalent amount of Ox or Red.

The first spectrophotometric methods used Co(II)-EDTA [67], Tyrol [59], methyl red [60], bromide ions [61] or Fe^{2+} [62] as reducing agents. Second methods with a reducing Fe(II) agent [24] as well as a method using iodide ions [56] were later developed.

- *Tiron [59], methyl red [60], bromide ions [61] and Fe(II) as reducing agents [62]*

The sample dissolving and reduction of Cu (III) are carried out in sodium acetate-acetic acid buffer [59], hydrochloric [60] or hydrobromic acid [61,62]. The analytical function is calibrated with the standards: $\text{K}_9\text{Cu}(\text{TeO}_6)_2$ [67, 59], YBCO superconductor [60,61] or Fe(II)-1, 10-phenantroline [62].

These methods have the following disadvantages: 1) the sample dissolving in acetate medium [59] is a continuous process; 2) The calibration with copper tellurium is not appropriate [67,59] because the teluratrite ions also exhibit oxidizing properties [65]; 3) It is not recommended to use the bromide ions as reducing agent because the liberated bromine is toxic [61]; 4) It is not appropriate to use a

superconductor [60] as calibration standard because there are problems with its precise oxygen coefficient determination; 5) The method using Fe(II) as reducing agent is not direct. The residual amount of Fe(II) is determined.

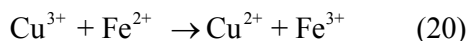
- *Cobalt (II) reducing agent [67,63]*

According to the method given in [67] the sample is dissolved in air, in a medium of sodium acetate-acetic acid buffer ($\text{pH} = 4.2 \div 4.7$), Co(II) and EDTA. A color complex of Co(III)-EDTA is formed, its absorbance is measured and the content of Cu(III) is calculated. But the method possesses some shortcomings: the sample is slowly dissolved (2-3 h); precise measurement of the sample mass is necessary in order to calculate Cu(III) content; the secondary standard $\text{K}_9\text{Cu}(\text{TeO}_6)_2$ is used to calibrate the function $A = \epsilon bC$.

Later, a new method for determination of non-stoichiometric oxygen content in YBCO bulk sample using Co(II) as reducing agent was developed [63]. The sample is dissolved in the presence of chloride ions, Co (II) and EDTA, without removing the air from the solution. The pH of the solution is 2.5. Co(III)-EDTA and Cu(II)-EDTA complexes are formed in a medium of sodium acetate-acetic acid buffer ($\text{pH} = 4.9$) and their absorbance is measured. The innovations of the method are: dissolving the sample in less acidic solution for about 2 minutes; formation of Cu(II) - EDTA complex and measuring its absorbance; calculation the δ non-stoichiometric oxygen coefficient as a ratio of the concentrations of Co(III) - EDTA and Cu(II) - EDTA complexes; using salts CoF_3 and CuSO_4 as standards for calibrating.

- *Iron (II) ions reducing agent [42]*

The sample is dissolved in hydrochloric acid (1 mol l^{-1}) in the presence of Fe(II) in the absence of air, under vacuum [24]. The oxidation-reduction reaction is carried out and the liberated amount of Fe(III) is equivalent to the amount of Cu(III) (Eq. 20).



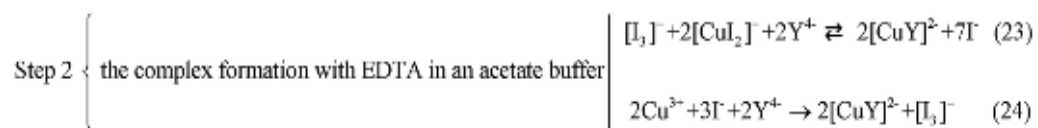
The absorbance of the yellow colored chloride complex of Fe(III) is measured at $\lambda = 335 \text{ nm}$ and the amount of Cu(III) in percentage is calculated. The coefficient of the analytical function is found by calibration with standart solution of Fe(III) in a hydrochloride acid medium.

- Reducer iodide ions [56]

Method [56] offers simultaneous determination of the oxygen coefficient and the total copper of YBCO superconducting materials. The sample is dissolved in a hydrochloride acid medium under inert atmosphere in the presence of large excess of potassium iodide so that a complex of $[\text{CuI}_2]^-$ instead of a precipitate of CuI is formed. Reactions take place as follows:



After sample dissolving the pH of the solution raise to 4.9 ± 0.1 and a solution of EDTA (H_4Y) is added. In the solution undergo processes like these in the method based on two consecutive iodometric titrations [47,48]. EDTA binds the Cu(II) ions in a stable complex (Eq. 23). The liberated iodine (Eq. 21) also interacts with CuI_2^- by Eq. 23. The equation of the total reaction (sum of Eq. 21 and (3) is given in Eq. 24.



From Eq. 24 follows that at pH 4.9 and in the presence of EDTA the total amount of copper (Cu(II) + Cu(III)) in the solution is bound in complex with EDTA and the remaining iodine is equivalent only to Cu(III) (Eq. 24): $n_{\text{I}_3^-} = \frac{1}{2} n_{\text{Cu(III)}}$

The amounts of Cu(III) and the total copper are determined by measuring the absorbance of the yellow colored complex of $[\text{I}_3]^-$ ($\lambda = 430 \text{ nm}$) and the $[\text{CuY}]^{2-}$ complex in blue ($\lambda = 730 \text{ nm}$). The oxygen coefficient δ is calculated by one of the two equations:

$$\delta = 1.5 \frac{(A_1 - a_1)b_2}{(A_2 - a_2)b_1} \quad (25) \quad \text{or} \quad \delta = \frac{M_{\text{YBCO}}(A_1 - a_1)V}{2mb_1 - M_0(A_1 - a_1)V} \quad (26)$$

where A_1 and A_2 are the absorbances measured at 430 and 730 nm, respectively; a_1 and b_1 coefficients are the intercept and the slope of the calibration function $A = f(C_{[\text{I}_3]^-})$; a_2 and b_2 are the coefficients of the function: $A = f(C_{\text{Cu(II)}})$, V – the volume of the solution.

The method offers easy for implementation procedure using a solution of Cu(II) for calibration of analytical function and it does not require precise measuring of the sample mass.

2.6 Methods without Calibration of the Analytical Function

Calibration of the analytical function is a procedure which complicates the analysis and

increases its timing. It is also a source of systematic errors. For example if one uses inappropriately standard, the values of the coefficient of the analytic function and the analytical results would not be accurate.

The δ -coefficient can be calculated from the molar ratio of Cu(III) and total copper (Eq. 1) and due to that possibility two spectrophotometric methods [57,58] for the determination of the non-stoichiometric coefficient δ without calibration of the analytical function are developed. Both methods use the oxidation of the iodide ions by Cu(III) from YBCO samples and the absorbance measuring of $[I_3]^-$ complex by two solutions - with and without ligand for Cu(II).

The common in these methods is: 1) Dissolving of the sample in hydrochloric medium under inert atmosphere in the presence of KI. During dissolution iodine is liberated according reactions 21 and 22; 2) Measuring the analytical signal in solutions with and without ligand. The pH of the solution is 4.9, maintaining by sodium acetate-acetic buffer. In solutions with ligand a complex between Cu(II) and the ligand is formed (see Eq. 23 and 24) and the absorbance is proportional to $\frac{1}{2} n_{Cu(III)}$, while the absorbance of the solutions without ligand is proportional to $\frac{1}{2} n_{Cu(III)} + n_{Cu(II)}$; 3) Using eq. 1 for calculating δ -coefficient. The ratio between the absorbances of the solutions with ligand and without ligand participates in the equation for δ -coefficient calculation; 4) The mass of the sample taken for analysis is about 10 mg.

The differences between the two methods are: 1) The first method [57] uses EDTA as ligand, the second [58] – glycine; 2) The solutions for measuring the analytical signal in the first method are two (with and without EDTA), in the second – three (one solution without glycine (2 ml sample solution) and two with glycine (2 and 5 ml of sample solution) are prepared); 3) The potassium iodide in the first method is introduced in hydrochloric acid. In the second method KI is introduced in dry vessel (the sample is in glass hemisphere placed in the vessel), the oxygen is removed and the hydrochloric acid in dropping funnel previously purged with inert gas is added to the vessel. Thus, the possible oxidation of the iodide ions from the air is eliminated [58]; 4) In the second method a blank sample passing through all stages of the dissolution process is prepared along with the sample dissolution. For this aim the experimental equipment for sample dissolution is accomplished. Two sets of dropping funnel, dissolution vessel and electromagnetic stirrer

are used (Fig. 1). Volumes of blank sample are introduced in the solutions for absorbance measuring, so that the sum of volume of YBCO and blank samples is always equal to 5 ml. Therefore the ionic strength and quantity of the KI in the three solutions are constants.

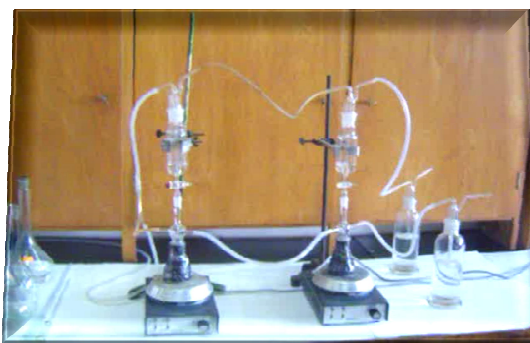


Fig. 1. Experimental equipment for sample dissolving [57]

Spectrophotometric methods for determination of oxygen stoichiometry in YBCO ceramics using iodide ion as reducing agent are summarized in Table 2.

It has to be noticed that the spectrophotometric method using glycine as ligand has been applied in order to determinate the oxygen stoichiometry of calcium replaced $RE_{1-x}Ca_xBa_2Cu_3O_y$ ($RE = Y, Eu, Er, Gd; x = 0, 0.2, 0.25, 0.3; y = 6.5 - x / 2 + \delta$) superconducting ceramics [71]. The relationships between critical temperature (T_C), oxygen content (y) and the calcium supplement (x) in the cited materials are given in Fig. 2. The method using the Co(III)-EDTA complex was also applied to determinate the oxygen stoichiometry of the above $RE_{1-x}Ca_xBa_2Cu_3O_y$ ($RE = Y, Eu, Er, x = 0, 0.2, 0.25$) superconducting ceramics. The relationships between the physical parameter T_C and oxygen content (y) and the calcium supplement (x) of these ceramics are present in Fig. 2. One can see that the values of the oxygen content “ y ” determined by both methods are not significantly differing. The analysing with the new method shows that the increase of the calcium content in the samples leads to a decrease of the T_C – value and the oxygen content (y) (Fig. 3). Decreasing of the T_C – value and the oxygen content (y) for the erbium system is especially critical.

Table 2. Iodometric methods for determination of oxygen stoichiometry of YBCO bulk samples; msample = 100 mg

Sample dissolving	Measurement of the analytical signal	Mole ratios of the reactions of dissolution and titration	Formula for calculation of δ
Two samples in a hydrochloride medium: (Procedure 1) under atmospheric conditions, and (Procedure 2) under inert atmosphere in the presence of KI [38-40].	<p><i>Procedure 1.</i> Iodometric titration of the total copper</p> <p><i>Procedure 2.</i> Titration of iodine, equivalent to the sum: $n_{\text{Cu(II)}} + 2n_{\text{Cu(III)}}$.</p>	<p><i>Procedure 1</i></p> $n_{\text{I}_2} = \frac{1}{2}(n_{\text{Cu(III)}} + n_{\text{Cu(II)}}); n_{\text{Na}_2\text{S}_2\text{O}_3} = n_{\text{I}_2}$ <p><i>Procedure 2</i></p> $n_{\text{I}_2} = \frac{1}{2}n_{\text{Cu(II)}} + n_{\text{Cu(III)}}; n_{\text{Na}_2\text{S}_2\text{O}_3} = n_{\text{I}_2}$	$\delta = 1.5 \frac{V_2^{\text{eq}} - V_1^{\text{eq}}}{V_1^{\text{eq}}}$
A sample in a hydrochloride medium under an inert atmosphere in the presence of KI [47].	<p>Two successive titrations of I_2 with a solution of $\text{Na}_2\text{S}_2\text{O}_3$.</p> <p><i>Titration 1.</i> Acetate medium (pH 4.8) in the presence of EDTA.</p> <p><i>Titration 2.</i> Hydrochloride acid medium after adding of extra H_2SO_4 and KI.</p>	<p><i>Titration 1</i></p> $n_{\text{I}_2} = \frac{1}{2}n_{\text{Cu(III)}}; n_{\text{Na}_2\text{S}_2\text{O}_3} = n_{\text{Cu(III)}}$ <p><i>Titration 2</i></p> $n_{\text{I}_2} = \frac{1}{2}(n_{\text{Cu(III)}} + n_{\text{Cu(II)}});$ $n_{\text{Na}_2\text{S}_2\text{O}_3} = 2n_{\text{I}_2}$	$\delta = 1.5 \frac{V_1}{V_2}$ <p>or</p> $\delta = \frac{M_{\text{YBCO}} C_{\text{st}} V_1}{2m - M_{\text{O}} C_{\text{st}} V_1}$

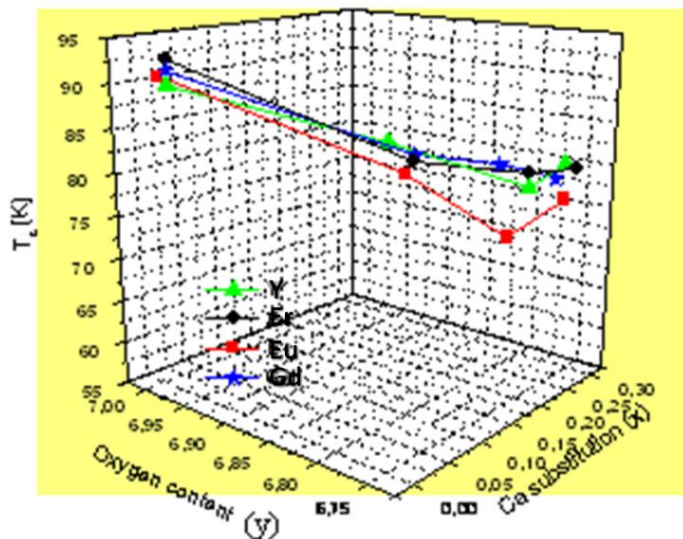


Fig. 2. Dependence of the critical temperature (T_c) from and the oxygen content (y) and the calcium supplement (x) in REBCO samples [71]

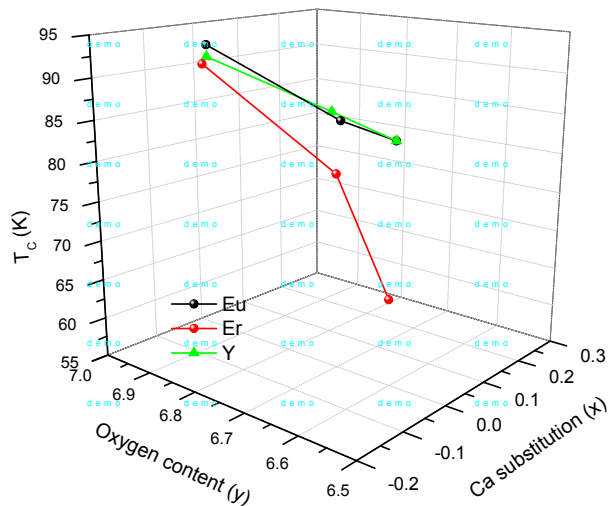


Fig. 3. Dependence of the critical temperature (T_c) from and the oxygen content (y) and the calcium supplement (x) in REBCO samples determining by the method using Co(III)-EDTA complex

Beside the discussed two spectrophotometric methods without calibration of the analytical function, a third method for determination of the oxygen stoichiometry with reducer iodide ions has been developed [73,74]. The procedure for analysis is similar to this of the method using glycine as ligand for Cu (II) [58]. The main innovation of the procedure is in adding a starch to the solutions for measurement of the analytical signal. The starch binds the liberated $[I_3]^-$ in a

stable colored compound which molar absorptivity at $\lambda = 545$ nm is about ten times higher than that of $[I_3]^-$ complex. Thus the sensitivity of the method has increased 10 times and the sample mass for analysis has decreased to 1-2 mg.

The novelty of this method is its application for determining not only high but also low values of δ -coefficient. This is achieved by changing the

volumes of the sample solution, taken for preparing the three solutions for measurement of the absorbance. In order to receive accurate and precise results for δ -coefficient when its values are from 0.2 to 0.5, the volumes of the sample solution must be 1; 1 and 5 ml. If the δ -coefficient values are higher (about 0.5) 2; 2 and 5 ml of sample solution can be used.

3. CONCLUSIONS

The literature review of the methods for analytical control of oxygen content in YBCO ceramics shows that the destructive methods, the methods for analysis of average sample are more frequently used than the non-destructive. The methods in solution: iodometric titration and spectral methods are preferred than volumetric and thermo-gravimetric methods. Furthermore, with the "wet method" the value of δ -coefficient correlated with the superconducting properties is defined. The volumetric and thermo-gravimetric methods determine only the total oxygen coefficient y ($y = 6.5 + \delta$).

During the past few years the superconducting materials have been used in electronics in the form of thin films upon substrates, in which the mass of the superconducting material is too low (less than 1 mg). The highest sensitivity from the spectrophotometric methods pass the methods using $[I_3]^-$ -starch compound for measuring the absorbance and those based on measuring the absorbance of Co(III)-EDTA pass highest sensitivity. The analysis is carried out with a small sample mass (1-2 mg), which is a good solution because of the high cost of the superconductors. Both methods do not require accurate measurement of the sample mass. This advantage, as well as the small sample mass, give the methods the possibility to be applied for determination of the oxygen stoichiometry of YBCO materials deposited as a thin film as set on substrates.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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