

Comparative evaluation of methods for precise determination of oxygen stoichiometry in high T_c oxides

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Abstract. A comparative study of the methods for oxygen stoichiometry—direct inert gas fusion method and two indirect iodometric methods—has been carried out. The indirect iodometric method in which Cu(III) is directly estimated, has been found to be more precise. Several samples of $\text{YBa}_2\text{Cu}_3\text{O}_x$ of varying x , their fluorine-substituted counterparts and also $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ and $\text{Tl}_2\text{Ba}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ have been analysed.

Keywords. Oxygen stoichiometry; oxide superconductors; thermogravimetry; inert gas fusion; iodometric methods.

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1. Introduction

Recently, there has been a worldwide interest in the preparation and characterization of a variety of superconducting oxides. The superconducting property of these oxide systems has generally been considered to be related to their oxygen stoichiometry (Cava *et al* 1987; Jorgensen *et al* 1987). The existence of a tetragonal to orthorhombic phase transition during oxygen annealing procedures is also known (Kini *et al* 1987). Thermogravimetric methods (TG/DTA) in air, oxygen, argon or hydrogen atmospheres, iodometric titration methods (Kishio *et al* 1987; Harris and Hewston 1987; Appelman *et al* 1987) and inert gas fusion technique (Takayama *et al* 1987; Ono *et al* 1987) have been used for the estimation of oxygen in these systems. The TG method has several limitations. It is an indirect method in which change in weight is measured as a function of temperature and this is assumed to be related to oxygen stoichiometry, presuming no other volatile loss. It assumes either an initial oxygen composition if an oxidising atmosphere is used or a final composition in case of a reducing atmosphere. Also, neither the loss of co-adsorbed $\text{H}_2\text{O}/\text{CO}_2$ nor the decomposition of any unreacted carbonates during TG heating can be accounted for. Uncertainty of the reaction products in hydrogen reduction and errors due to the presence of any free CuO are other complications. Also the TG methods are known to have poor precision. Compared to other aspects of characterization, studies on other analytical methods for oxygen stoichiometry are fewer. The present work was carried out to comparatively evaluate these analytical methods as regards their precision and accuracy and applicability based on a variety of samples. Results have been compared between the inert gas fusion method and iodometric methods and the applicability of these methods

to achieve high precision/accuracy for oxygen determination was assessed using a variety of samples containing 1, 2, 3 type oxides and their partially fluorinated counterparts.

2. Experimental

The inert gas fusion was performed in LECO-136 oxygen determinator. The carbon monoxide produced by the fusion of the specimen in graphite crucible was estimated by infra-red measurements in this equipment. About 8–10 mg of the samples was weighed to 0.01 mg, enclosed in a tin foil, placed inside a nickel wire basket flux and analysed. The analytical values were corrected for blanks due to tin foil and nickel wire flux.

Iodometric titrations were carried out on lines similar to those done by earlier workers, using an A grade burette with 0.01 ml calibrations. The thiosulphate solution was standardized against a standard copper solution prepared from electrolytically pure copper.

The fluoride content of the samples was estimated by dissolving the sample in perchloric acid and distilling the hydrofluo-silicic acid by the distillation method (Willard and Winter 1933) and collected in sodium hydroxide. The fluoride content was determined using a fluoride ion sensitive electrode (Radiometer make F 1052 F) and a meter (Radiometer PHM 64).

The oxide and fluorinated oxide compounds were prepared and supplied by the Chemistry and Water Chemistry Divisions of this Centre respectively. All reagents used were of analytical grade.

3. Results and discussion

3.1 Inert gas fusion method

This is a direct method for the estimation of oxygen and the initial validation of the method for oxides was established by analysis of freshly ignited Y_2O_3 . Replicate values of 20.71, 21.61, 21.32 and 21.81% with a mean of $21.36 \pm 0.48\%$ were obtained (the uncertainty is expressed as \pm one standard deviation, a measure of precision). The mean value compared well with the theoretical value of 21.26%.

Replicate estimation of oxygen in a $YBa_2Cu_3O_x$ specimen (heated at $950^\circ C$ for 72 hours and slow cooled in oxygen and preserved in a desiccator) was carried out and the oxygen values obtained were 17.56, 16.57, 16.95, 17.73, 17.57, 16.78 and 17.72% with a mean of $17.26 \pm 0.49\%$ (relative standard deviation of 2.8%). The precision is of the same order as that for pure Y_2O_3 . This mean corresponds to an oxygen coefficient of ~ 7.3 , a value higher than expected.

These values point out the shortcomings of this method: (i) since this method determines oxygen directly, it is sensitive to the presence, if any, of all oxygen-bearing species — moisture, carbonates, unreacted oxides etc. and this may explain the higher value obtained. In this respect, it is similar to the TG method. (ii) As the method is primarily meant for low oxygen containing materials such as metals and alloys, application of this method to oxides necessitated analysis of very small amounts of the sample, contributing to errors in weighing. (iii) Although the standard deviation

relative to the mean is only 3%, the absolute scatter of values is rather wide ($\sim 1\%$ absolute between the extreme values). This is the same order as the difference expected between the theoretical values of oxygen in say $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ and $\text{O}_{7.0}$. Hence it is concluded that this method cannot distinguish between the stoichiometries such as the above.

3.2 Iodometric methods

The method of Harris and Hewston (1987) involves two titrations, one to estimate the total copper content as Cu(II) and the other to determine Cu(III) + Cu(II), by dissolving the sample in hot HCl followed by the addition of KI or by dissolving the sample in HCl + KI and estimating the liberated iodine in both the cases. The fraction of Cu in trivalent state is calculated. In Appelman's modification (hereafter referred to as the modified method), which involves only a single titration, the Cu present in the specimen as Cu(III) is exclusively estimated by dissolving the sample in cold HBr with subsequent addition of KI. The addition of citrate results in complexing copper in Cu(II) state, and the iodine liberated due to reduction of Cu(III)–Cu(II) is estimated. In both the methods, oxygen stoichiometry is calculated based on the known metal stoichiometry. Thus both are indirect methods of estimating oxygen stoichiometry.

The same specimen which was analysed by the inert gas fusion method was analysed by both these methods and the results of replicate analyses are given in table 1.

Experimental data in table 1 show that though both methods give the same mean value, the latter has a significantly higher precision. The variations in the latter method are in the third decimal place as against the second decimal place variations in the former. The modified HBr dissolution method of Appelman is preferred because of its simplicity and higher precision. It is also easier, experimentally since it has one titration less and can be done in ambient air, avoiding the use of argon atmosphere. The modified method has two inherent advantages: (i) citrate keeps copper complexed in the Cu(II) state preventing further reduction to solid Cu(I) iodide, estimating only Cu(III)—thus insensitive to the presence of any free CuO; (ii) initial dissolution of the sample in 4 M HBr and the subsequent conversion of bromine (formed by the reduction

Table 1. Analysis of $\text{YBa}_2\text{Cu}_3\text{O}_x$.

Iodometric method* (Harris and Hewston 1987)	Modified method**
6.769	6.773
6.752	6.773
6.790	6.777
6.791	6.784
6.766	6.781
6.799	
6.763	
6.776	6.778
± 0.018	± 0.005

*Sample weight: 60–80 mg. **Sample weight: 40–50 mg.

of Cu(III)) to iodine at a much lower acidity minimizes copper catalysed oxidation of iodide by atmospheric oxygen.

The accuracy of the modified method was also verified by experiments in which 0.2 mmol of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ along with KBrO_3 was substituted for the unknown samples. The results are summarized in table 2.

Several $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples were analysed by the modified method and some typical results are given in table 3. The six replicate analyses of specimen 1 confirmed the higher precision. The numbers 2–5 show the ability of the method to distinguish different oxygen stoichiometries between the close range of 6.5 to 7.0 (which would not have been possible by the fusion method). Specimen 6 was a tetragonal sample and gave no titre value.

This method could be easily extended to bismuth-based superconducting oxides. Initial experiments on specimen 1, when repeated in the presence of Bi_2O_3 gave the same expected oxygen stoichiometric value indicating that Bi(III) does not interfere in the method. Specimens 7 and 8 are of two different compositions (of oxygen stoichiometry $5.5 + \delta$ and $8 + \delta$ respectively). Analysis of bismuth compounds did not present any problems.

When this method was tried on thallium-bearing superconducting oxide, problems were encountered. During the dissolution in HBr , Tl(III) was reduced to Tl(I) liberating

Table 2. Accuracy of the modified method.

KBrO ₃ , mg			
Taken	Found	Error (mg)	% error
1.874	1.869	-0.005	-0.27
1.874	1.883	+0.009	+0.48
0.937	0.941	+0.004	+0.43

Table 3. Iodometric analyses of superconducting oxides.

Sl. No.	Compound	x^a
1	$\text{YBa}_2\text{Cu}_3\text{O}_x$	6.887, 6.881, 6.886 6.884, 6.882, 6.888 (6.885 ± 0.003)
2	-do-	6.657, 6.656
3 ^c	-do-	6.856, 6.857
4 ^c	-do-	6.873, 6.879
5 ^c	-do-	6.902, 6.887
6	-do-	6.500 ^b
7	$\text{BiSrCaCu}_2\text{O}_x$ (5.5 + δ)	5.683, 5.682
8	$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_x$ (8 + δ)	8.156, 8.153

a, assumes the metal composition as given in the corresponding formula; b, tetragonal, no iodine liberated; c, similar to No. 2, but with Bi_2O_3 present (0.1–1%).

free bromine in a manner similar to $\text{Cu(III)} \rightarrow \text{Cu(II)}$. This was confirmed by analysing Tl_2O_3 as a sample. When systems like $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_x$ were analysed, it was only possible to say that the titre value represents the number of moles of Cu(III) plus half the number of moles of Tl(III) . Hence, in its present form, the method is not applicable to thallium-copper compounds.

3.3 Analysis of fluorinated oxides

Recently, fluorine-substituted 1, 2, 3 compounds have also been studied for their superconducting properties (Rao *et al* 1988). No work on the estimation of oxygen and fluorine stoichiometry in such compounds has yet been reported. The present iodometric method was successfully extended with suitable modification in the calculations. Assuming a general formula of $\text{YBa}_2\text{Cu}_3\text{O}_{x-0.5y}\text{F}_y$ and two simultaneous equations y and x involving two experimental values E (mole of thiosulphate consumed per gram of the sample) and F (weight % fluorine in the sample).

$$\frac{(19y)(100)}{(554.21) + (x - 0.5y)16 + (19y)} = F \quad (1)$$

and

$$\frac{13 + E(554.21 + 11y)}{(2 - 16E)} = x. \quad (2)$$

Equation (2) is derived on lines similar to that of Appelman's equation suitably modified. Solving for x and y ,

$$y = \frac{-1313.42F}{22F + 30400E - 3800} \quad (3)$$

and

$$x = \frac{1900y - 11Fy - 554.21F}{16F}. \quad (4)$$

Table 4 summarizes the results of analyses of some fluorinated oxide samples by the above modification.

Table 4. Analysis of fluorinated oxides.

Sl. No.	$\text{YBa}_2\text{Cu}_3\text{O}_{x-0.5y}\text{F}_y$				
	E Mole of thiosulphate consumed/g of sample	F Fluorine content wt%	x	y fluorine stoichiometry	$(x - 0.5y)$ oxygen stoichiometry
1	4.47×10^{-4}	6.8	6.56	2.46	5.33
2	4.91×10^{-4}	4.9	6.57	1.75	5.69
3	7.62×10^{-4}	2.2	6.66	0.77	6.28
4	4.12×10^{-4}	18.0	6.56	6.97	3.07

4. Conclusions

The drawbacks of the TG methods are already known and documented. The inert gas fusion method does not have sufficient precision to distinguish close oxygen stoichiometries. Also higher oxygen values are obtained due to contribution from other oxygen-bearing species. Though both the iodometric methods give values which agree with each other, Appelman's method has a much higher precision, is elegant and easy to carry out. It can easily distinguish between close oxygen stoichiometries. Its utility has been established by the analysis of a variety of samples including bismuth compounds. The iodometric method has also been successfully extended to analyse fluorinated oxides.

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