

REVIEW ARTICLE

DETERMINATION OF TRACE IMPURITIES
IN MATERIALS

D C PARASHAR

*NPL-DoE Centre for Characterization of Materials for Electronics,
National Physical Laboratory, New Delhi-110012, India*

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Research work done at the National Physical Laboratory to develop new methods which are more specific and/or more sensitive has been reviewed. These methods are based on the use of existing facilities viz. atomic absorption spectrophotometry, uv-visible spectrophotometry, gas chromatography and conventional chemical methods. It is possible to determine impurities like boron at 5ppb level, phosphorus at 100ppb and oxygen non-stoichiometry in 1:2:3 compounds with higher accuracy. Boron is determined spectrophotometrically by forming a complex with curcumin and phosphorus is determined indirectly by atomic absorption spectrophotometry by forming phosphomolybdate complex with antimony or bismuth which have 1:1 ratio with phosphorus in the complex.

Gas chromatographic technique has been used to evaluate the oxygen non-stoichiometry in high temperature superconductors (1:2:3 compound) where the HTc sample is dissolved in dilute nitric acid in helium environment and the oxygen released is determined using thermal conductivity detector.

Key Words: Trace Impurity Analysis; Atomic Absorption Spectrometry;
UV-visible Spectrophotometry; Gas Chromatography

Introduction

Determination of trace impurities in various materials has played an important role in the understanding and advancement of science and technology. Improvement in the quality of materials and capability to analyse them go hand in hand. With the progress in industrialization and advancement in our understanding of the role of impurities or minor constituents at trace and ultra trace levels is building up more and more pressure on the analytical scientists to develop new methods which are more sensitive, specific and less time consuming. Certain impurities at parts per trillion (10^{-12}) concentration are known to adversely affect the minority carrier life time in silicon and make fluoride glass unsuitable for optical fibre for long wavelength transmission¹.

Nearly all the physical and chemical properties characteristic of a particular element or compound are made the basis in modern instrumental for the determination of impurities at trace and ultra trace concentration. Instruments based on atomic absorption, atomic emission and mass characteristics manufactured by various companies have become popular and have enhanced capability of ultra trace analysis². Atomic absorption spectrometer is relatively low-

er in cost and superior in sensitivity for most of the metallic elements with only a few exceptions.

The technique of atomic absorption spectrophotometry provides freedom from interference in addition to high sensitivity for the determination of the metallic impurities in material characterization. Few impurities like Mg, Zn, Ag, and Cd can be determined at ppt concentration and some at ppb and most at ppm concentrations. High sensitivity and relatively low cost has made atomic absorption spectrophotometry a popular tool in the hands of analytical chemists. New methods are being developed to improve sensitivity and also to determine those impurities which have their resonance absorption lines in the far ultra violet/vacuum ultra violet region and atmospheric absorption causes serious interference. The other commonly used equipments in most of the analytical laboratories are uv-visible spectrophotometer and gas chromatograph. Some of the recent results obtained at the National Physical Laboratory using these facilities are reviewed here.

Indirect Method for the Determination of Phosphorus by Atomic Absorption Spectrophotometry

Traces of phosphorus are generally determined by spectrophotometric method based on the formation of phosphomolybdate which is selectively reduced to yield molybdenum blue. However, careful control of various parameters like pH, concentration of reducing agent etc. are essential to achieve selective reduction as the molybdate ions interfere in the colour formation. Atomic absorption spectrophotometry is often preferred over uv-visible spectrophotometry for the determination of elements due to freedom from interferences from associated metal ions. However, phosphorus is not easily determined by atomic absorption spectrophotometer as the resonance line of phosphorus lies in the extreme ultraviolet region. Indirect methods^{3,4} have been developed in this laboratory for the determination of phosphorus. 25 to 50 mg of sample taken in a 50 ml Erlenmeyer flask and 5 ml of dilute nitric acid (1:1) is added. The solution is heated to dissolve all the sample. Heated nearly to dryness. Two or three ml of perchloric acid (60%) and a few drops hydrofluoric acid are added and the solution is heated to fuming stage. The solution is heated gently on a hot plate until perchloric acid started refluxing on the walls of the flask and then heated to strong fumes. This indicates the complete removal of nitric acid and silica as silicon tetrafluoride (SiF_4). The phosphorus at this stage is converted to *ortho* phosphates. The solution is cooled and 10ml each of distilled water and 10% sodium sulphite solution are added. The solution is boiled for 2 to 3 minutes for complete removal of unreacted sodium sulphite. Any turbidity is removed by filtration. Few drops of ammonia added to remove excess acidity. 8 ml of mixed reagent made by mixing 125 ml of 5N H_2SO_4 , 37.5 ml of 4% ammonium molybdate, 75 ml of 1.5% ascorbic acid and 12.5 ml of 0.001 M solution of potassium antimonyl tartrate is added and the solution is diluted to 25 to 30 ml. After ten minutes the phosphomolybdate complex is extracted by 25 ml of methyl isobutyl ketone. The molar concentration of antimony determined by atomic absorption spectrophotometer at 206.8 nm gives

the molar concentration of phosphorus in the solution.

The method has been successfully employed for the determination of phosphorus in steels³, chlorosilanes⁴ and semi conductor grade silicon⁵ and the results are tabulated in Tables I to III.

Table I
Determination of phosphorus in standard steel

Standard steel	Type of steel	Certificate value (%)	Phosphorus found(%)	Error %
1. B.C.S. No. 232	Carbon steel	0.076	0.074	-0.002
2. B.C.S. No. 163	-do-	0.049	0.048	-0.001
3. B.C.S. No. 235	Stainless steel (Cr 19.0% Ni 8.73%)	0.020	0.020	Nil
4. B.C.S. No. 224	Carbon steel	0.012	0.011	-0.001
5. B.C.S. No. 241/1	High speed (W-19.6%)	0.021	0.021	Nil

Table II
Determination of phosphorus in chlorosilanes

Sample No.	Sample	Phosphorus added in (ppm)	Phosphorus (ppm)		Difference in ppm
			Expected	Obtained	
1.	Trichlorosilane (1)	1	2.48	2.52	+0.04
2.	Trichlorosilane (2)	1	1.62	1.65	+0.03
		2	2.62	2.64	+0.02
3.	Tetrachlorosilane (1)	0.50	0.95	0.98	+0.03
		1.00	1.45	1.47	+0.02
4.	Tetrachlorosilane	0.50	0.82	0.80	-0.02
		1.00	1.32	1.36	+0.04

Spectrophotometric Methods

Very few spectrophotometric methods are acceptable for the determination of boron in high purity silicon. The boron curcumin complex formation is established in earlier formed using bismuth nitrate and sodium-molybdate in place of potassium antimonyl molybdate. The complex is extracted in methyl isobutyl ketone and phosphorus determined in terms of bismuth by measuring the molar concentration of bismuth at 223.06 nm. The detection limit of phosphorus is 0.02 ppm with standard deviation of 0.002 ppm.

Table III
Determination of phosphorus in semiconductor grade silicon

S.No.	Phosphorus added (ppm)	Phosphorus		Difference (ppm)
		Expected	Obtained	
1.	0.5	0.62	0.61	-0.01
2.	1.0	1.16	1.16	Nil
3.	0.5	0.60	0.59	-0.01
4.	1.0	1.06	1.05	-0.01

Table IV
Determination of phosphorus in silicon

S.No.	Sample	Phosphorus determined by standard method (ppm)	Phosphorus determined in terms of bismuth (ppm)
1.	High purity silicon prepared at NPL	5.6	5.6
2.	BDH silicon	50.5	50.0
3.	Semiconductor grade silicon	20.0	19.2
4.	Commercial silicon	57.0	56.8

The method has been applied for the determination of phosphorus in high purity silicon and copper metal. The results obtained with different silicon samples are given in Table IV.

Very few spectrophotometric methods are acceptable for the determination of boron in high purity silicon. The boron curcumin complex formation is established in earlier work⁸⁻¹¹. In the present investigation, the method established a very specific and selective condition for the determination of boron with curcumin¹². Boron forms a reddish brown complex with curcumin in sulphuric and acetic acid mixture (1:1). The complex shows maximum absorbance at 545 nm and Beer's Law is obeyed upto 0.2 ppm of boron. The molar absorptivity 1.54×10^5 proves the sensitivity of the method. The interference of copper, cobalt, nickel, manganese, magnesium, iron, aluminium, chromium, arsenic, antimony, bismuth, titanium, vanadium, molybdenum, phosphate, nitrate, nitrite, fluoride, chloride and perchlorate has been studied and it has been found that 100-fold excess of these ions do not interfere in the determination of boron.

A measured quantity of boron solution, 1 ppm standard in 1:1 H_2SO_4 and Glacial acetic acid was taken in a 50 ml polythene beaker and a definite amount of acid mixture was added (by a burette) to make the solution to 3 ml. Exactly 3 ml of 0.125% curcumin in glacial acetic acid solution was added, mixed thoroughly and the mixture was kept in the dark for at least 2 hours. Then 15 ml of ammonium acetate acetic acid buffer solution was added and transferred in a 50 ml volumetric flask and volume was made to 50 ml with 1:1 acetone water mixture. The absorbance was measured against a reagent blank which was prepared under identical conditions with the same quantity of reagents. The pH of the final solution was nearly 1.7.

Absorbance curves of the boron-curcumin complex containing varying concentration of boron ranging from 0.01 ppm to 0.08 ppm are shown in Fig. 1.

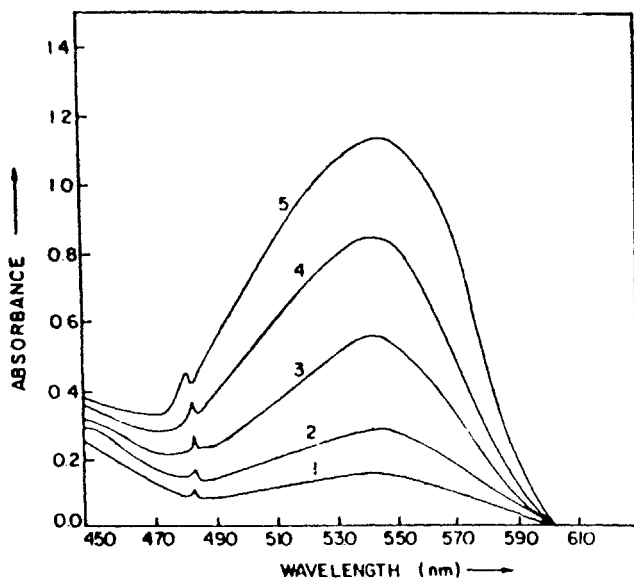


Fig. 1 Absorbance curve of Boron-curcumin complex, concentration of boron(I) 0.01 ppm (2) 0.02 ppm (3) 0.04 ppm (4) 0.06 ppm (5) 0.08 ppm

The boron curcumin complex formation is satisfactory when the acidity is controlled with 1.5 to 2 ml of 1:1 H_2SO_4 and glacial acetic acid mixture so that the final pH of the solution remains within 1.0 to 2.0.

The method has been applied to silicon. 0.1 g of silicon is dissolved in 2-3 ml of electronic grade hydrofluoric acid, 3 to 4 ml of electronic grade nitric acid and 1 ml of 0.1% mannitol in platinum dish heated on a water bath. The solution is evaporated to dryness and the residue dissolved in a few drops of hydrochloric acid. Acid mixture is added and colour developed with curcumin solution and measured at 545 nm. The method has been applied for the determination of boron in semiconductor grade silicon and borophosphosilicate glass films. The results obtained for silicon are given in Tables V & VI.

Table V
Determination of boron in silicon

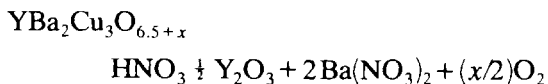
Sample No.	Boron added	Boron (ppm)		Difference (ppm)
		Expected	Obtained	
1.	0.10	0.15	0.15	0
2.	0.05	0.17	0.18	+ 0.01
3.	0.10	0.190	0.195	+ 0.005
4.	0.10	0.23	0.226	- 0.004

Table VI
Determination of B in borophosphosilicate glass

Sample No.	Boron added (ppm)	Boron (ppm)		Difference (ppm)
		Expected	Obtained	
DC 1	2.0	15.4	15.4	Nil
DB 1	5.0	16.5	16.48	- 0.02
DB 2	2.0	14.0	14.0	Nil
DB 3	5.0	13.78	13.76	- 0.02

Determination of Oxygen Non-Stoichiometry in HTc Superconductors

Methods involving the use of thermogravimetry^{13,14}, volumetry^{15,16}, iodometry¹⁴, infrared spectrometry¹⁷, and mass spectrometry¹⁸, have been used for the determination of oxygen in the Y-Ba-Cu-O system using the technique of gas chromatography¹⁹. The powdered sample, when reacted with dilute nitric acid, releases oxygen by the following reaction:



Twenty-five to 30 mg of the sample powder was placed in a small Pyrex boat and set on a glass spoon attached to the stopcock of the glass sampler (Fig. 2) designed for this work. Ten ml of (1:1) HNO₃ (mixture of one part of concentrated ARG nitric acid, sp. gr. 1.41 and one part of distilled water) was taken into the glass sampler and connected to the gas sampling valve with 1 cm³ loop of the gas chromatograph with automatic injection system in a closed

circuit as shown in Fig. 3. Soda lime U-tube to trap acid vapours, pulse-pump to homogenize the gas mixture, vacuum line to evacuate and helium gas to flush its atmosphere were used in the closed circuit. Perkin Elmer gas chromatograph model Sigma 2000 coupled with data station model 3700 and Epson FX-85 printer was used for the *in situ* determination of evolved oxygen. 12' × 1/8" S/S column containing molecular sieve 13 × (60-80 mesh) maintained at 35 °C, helium carrier gas flow at 30 cm³ min⁻¹ and hot wire detector (filament current 240 mA, range-3) were used for oxygen separation and its evaluation.

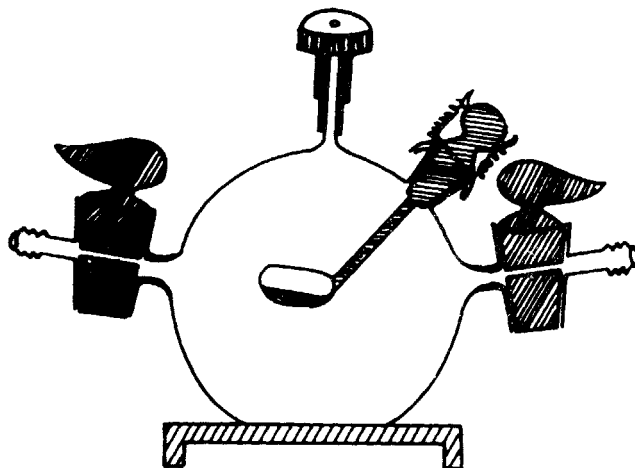


Fig 2 Glass Sampler for *in situ* evolution of oxygen

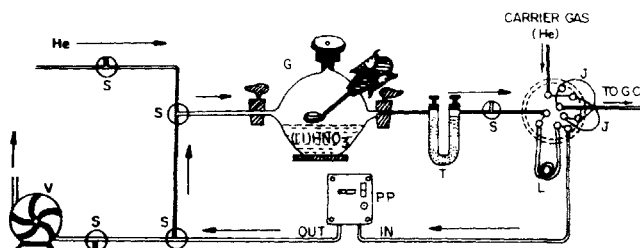


Fig 3 Schematic diagram of the closed circuit system. G-Glass Sampler, T-Sodalime U-Tube, L-1 cm³ loop of gas sampling valve, PP-Pulse-pump, V-Vacuum System, S-three way stopcock.

The circuit system was evacuated and flushed with helium gas and oxygen signal for the blank recorded. Sample boat containing weighed amount of HTc material was then dropped into the acid by rotating the stopcock by 180. Oxygen evolved in the sampler was circulated by the pulse-pump within the circuit. It took 20 to 30 minutes for complete evolution of oxygen from HTc sample. 1 cm of sample gas was injected into the gas chromatograph and signal recorded. The area of the oxygen peak computed by the data station when compared with the calibration curve prepared with known oxygen additions under identical conditions gave the volume of oxygen evolved from the sample. To

obtain calibration curve the circuit system (Fig. 2) along with the glass sampler which contained 10 ml (1:1) HNO_3 was partially evacuated and flushed with high purity helium gas. The atmosphere was brought to ambient pressure by releasing the excess pressure of helium into the atmosphere through three way stopcock (Fig. 2). The gas of the circuit was injected into gas chromatograph through 1 cm loop and oxygen signal for the blank was recorded. Known volumes of high purity oxygen were introduced into the glass sampler from top through self-sealing silicon rubber septum with the help of gas tight syringe. Oxygen-helium gas mixture was homogenized within the circuit by circulating it with pulse-pump. 1 cm of the gas mixture from the circuit was injected through loop into gas chromatograph and oxygen peak area recorded and corrected with blank. Five such observations for each oxygen addition were taken and the average area (coefficient of variation 2%) was calculated. Peak area versus oxygen volume (in cm) added into the sampler was plotted to obtain the calibration curve. The value of x was calculated after correcting for the ambient temperature and pressure.

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