

Spectrochemical Determination of Impurities in Rutile

by

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金紅石內에 포함된 不純物의 分光化學的 測定

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Abstract

A spectrochemical method for the determination of the major impurities, such as aluminum, iron, magnesium and silicon, in rutile single crystals and variously doped rutile is presented.

By applying higher current (12 amp) and a 1:2 sample-to-graphite dilution by weight, the elaborate sample preparation needed for conventional fusion technique was avoided, and relatively higher detection limits were established.

Average deviations are approximately $\pm 8\%$ for iron and magnesium in the concentration ranges of 0.007 to 0.7% and 0.006 to 0.6% respectively, and $\pm 5\%$ for aluminum and silicon in the range of 0.005 to 0.5%.

Introduction

Rutile single crystals are of interest as high dielectric-constant materials and semiconductors.⁽¹⁾ They are grown as boules by the Verneuil flame-fusion technique.^{2,3} An intensive study on their electrical and optical properties⁽⁴⁾ has been made in this laboratory. They are however still far from ideal: they are badly strained⁽⁵⁾ and contain impurities.⁶ The present experiment

attempts to determine the types and quantities of these impurities.

Chemical determinations of the principal impurity elements are very time-consuming and unreliable in the low concentrations in which they are generally found. Three common spectrographic techniques, solution,⁽⁷⁻¹⁴⁾ fusion,⁽¹⁵⁻¹⁶⁾ and solid-sample⁽¹⁷⁾, have been reported for the quantitative analysis of impurities in titanium metal, titania, titanium tetrachloride, and their intermediate products. For our present purpose the direct-sample method was employed because of its simplicity and rapidity.

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Experiments

Preparation of standard samples; Titanium dioxide powder of high quality, which has been prepared in this laboratory by decomposition of ammonium titanate sulfate,⁽¹⁸⁾ was selected as base material, since commercial titanium dioxide was found to be much less pure, having twice the Fe and three times the Si content. To give an initial standard, the oxides of the elements sought were weighed, and their weights to that of the base material adjusted to contain 1 weight percent of each of the oxides. Then 0.318 gram of this standard was diluted with 0.684 gram of the base material to give the second. Next 0.318 gram of this second standard was mixed with 0.684 gram of base material, giving the third standard. This operation was continued until the lower limit of concentrations is obtained. Such standards will dilute as follows: 1.0%, 0.316%, 0.1%, 0.036%, etc.⁽¹⁹⁾ To minimize the sampling error, the base material and the impurity oxides were screened through a 300 mesh sieve and thoroughly mixed in a mechanical shaker for five minutes for each preparation.

Subsequently, the standard samples were mixed with Specpure Graphite* in a 1:2 ratio, sample-to-graphite by weight. To grind these mixtures an agate mortar was used except in the case of silicon because of possible error introduced by the agate (a form of SiO₂). Here a tungsten carbide mortar was used.

Preparation of samples; Samples submitted for analysis were in the form of crystal boules. Each unknown sample was crushed in the mortar and small chips were selected for sampling under a microscope. Care had to be taken to avoid using surface chips from a crystal, since spectrographic tests showed the concentrations of impurities on the crystal surface to differ from

those within the crystal by a ratio of 5:1 in Al, 10:1 in Fe, 8:1 in Mg, and 4:1 in Si.

Samples were prepared by grinding the selected chips in the tungsten carbide mortar in the same manner as standard preparation. Previous experiments had shown the desirability of using a layer piece of crystal (3 to 6 grams) to obtain a more representative portion and to minimize the effects of segregation. Smaller samples resulted in greater variations, particularly in the cases of iron and magnesium.

Tungsten contamination from the mortar was not detected spectrographically within the established limits of 0.007% under the same experimental conditions.

Procedure; A d-c arc excitation was selected because of the detection sensitivity requirements. Various sample-to-graphite ratios, current values, exposure times, and electrode configurations were tried in searching for optimal conditions. In order to facilitate the melting of the crystal, which is a poor thermal conductor, a current of 12 amp was used. High dilution of the sample with graphite not only provided a stable burning arc but also prevented undesirable sputtering. The mixture of sample and graphite was packed into the crater (5mm depth) of the sample electrode which in the present experiment is an anode. The cathode is cone shaped with a planar cross section of 2mm at the base.

An improvement in the sensitivities of many elements can be achieved by taking advantage of selective volatilization of the impurities. Low-boiling elements are excited early in an exposure, but high boilers only toward the end of the exposure. By recording separately different segments of the exposure, higher impurity line-to-background ratios are obtained. This technique, however, was not applied to rutile crystal analysis because the standard samples which are mechanical mixtures differ from samples derived from crystals in particle size, density, chemical

* Obtained from National Carbon Company, Cleveland, Ohio.

bonding and impurity distribution.

Since there are those differences between the unknown and the standard samples, they were arced completely in order to minimize the lessening of sensitivity from these effects. In order to improve sensitivity, a few standard samples were studied by means of the solid-diffusion principle. A mechanical mixture of TiO_2 and impurity oxides (both fine powder) is calcined at 1300°C for 14 hours. The impurity oxides diffuse into and through the TiO_2 matrix. The volatility of each impurity element of the calcined mixture and the simple-mixture standard samples is under investigation.

A rotating four-step sector was used to read the intensities of the lines for different exposures.

It is important to replace the counter electrode (the cathode) with one having a freshly prepared tip for each exposure, as the formation of titanium dioxide on the tip causes erratic results.

Eastman Kodak I 1 N plates were used instead of 103-0 plates so as to eliminate the strong background radiation even though 103-0 plates are better generally for the region between 2500 and 5000 Å. Each plate, exposed for 5 seconds at 6 amp, was calibrated from the iron spectrum. The problem of selecting internal standards was avoided by taking titanium as an internal standard because the amount of titanium in both standard and unknown samples remains practically constant in this experiment. The analytical and the internal standard lines must be chosen so that the ratio of their radiant flux has minimal change with variations in the excitation conditions. Through the efforts of Moore,⁽²⁰⁾ and Convey and Hurwitz,⁽²¹⁾ selection of homologous spectral line pairs is possible by means of their excitation potentials (Table 1).

Since the properties of the photographic emulsion are not uniform, and widely separated lines may be located in an area of slightly different emulsion characteristics, the lines

Table 1. Analytical line pairing

Element	Spectral line	Excitation potential	Internal standard line	Excitation potential
Al	3092.713 Å	4.00	Ti 2644.234 Å	4.69
Fe	3020.640	5.11	Ti 2644.234 Å	4.69
Mg	2852.129	4.33	Ti 2644.234 Å	4.69
Si	2881.578	5.06	Ti 2644.234 Å	4.69

should preferably be of like wavelength and so close-spaced that local variations of photographic development will influence both of the lines. For this reason for the purpose of double checking, titanium-line and series of Table 2 was used.

Table 2. Analytical line pairing

Element	Analytical	Internal standard line
Al	3092.713 Å	Ti 3038.706 Å
Fe	3020.640	"
Mg	2852.129	Ti 2856.62
Si	2881.578	"

It was found, however, that the variations of the results from the selection of two different internal standard lines were tolerable within experimental error. This seems to be due to the difference in their excitation potentials and other properties.

A nonrecording densitometer was used to read the intensities of the lines. Corrections for background and residual impurities in the original sample were made and the rectilinear function between intensity and concentration plotted. Other experimental conditions are summarized in Table 3.

Treatment of data; The background correction⁽²²⁾ consists in converting line and background transmissions (or densities) into relative intensities and subtracting the background intensities from the line-plus-background intensities for both analyses and internal standard lines. It was found that the calibration curves of $\log I_{Fe}/I_{Ti}$, $\log I_{Al}/I_{Ti}$, $\log I_{Mg}/I_{Ti}$, and $\log I_{Si}/I_{Ti}$, versus $\log C$ (Fe, Al, Mg, and Si, respectively) are rectilinear after corrections for the background and residual

Table 3. Analytical conditions

Apparatus	Hilger large quartz and glass spectrograph
Excitation source	D. c arc, anode excitation
Amperage	12amp
Voltage	210 volts
Analytical gap	5mm
Spectral region	2300 to 4400 A
Electrode	cathode, National Carbon Co., Carbon L3866; anode, National Carbon Co., Graphite L 3803

impurities in the base material.

In determining the residual impurities in the starting material of titanium dioxide, the addition method of Harvey²³ was followed. Table 4 lists each standard series.

Table 4. Preparation of standards

Sample designation	Added %		Final %	
	Al	Fe	Al	Fe
C. W. N.	none	none	0.0060	0.0200
C. W. N. -A	0.0010	0.0032	0.0070	0.0232
C. W. N. -B	0.0032	0.0100	0.0093	0.0300
C. W. N. -C	0.0100	0.0316	0.0160	0.0516
C. W. N. -D	0.0316	0.1000	0.0376	0.1200
C. W. N. -E	0.1000	0.3160	0.1060	0.3360

	Added %		Final %	
	Mg	Si	Mg	Si
C. W. N.	none	none	0.0050	0.0200
C. W. N.-A	0.0032	0.0032	0.0082	0.0232
C. W. N. -B	0.0100	0.0100	0.0150	0.0300
C. W. N. -C	0.0316	0.0316	0.0366	0.0516
C. W. N. -D	0.1000	0.1000	0.1050	0.1200
C. W. N. -E	0.3160	0.3160	0.3210	0.3360

The resulting intensity ratios were plotted. It was found possible to draw a straight line through these five points, which could be extrapolated to zero intensity ratio; its intersection with percent iron ordinate was 0.020 unit below the original base line and thus indicated an iron content of 0.020% in the base material (Sample C. W. N.). This value was added to each of the addition standards to give the final percent val-

ues for each standard. Similar calculations were made for other elements.

Accuracy and precision; A comparison of the precision of results obtained by the conventional fusion and the present technique is shown in Table 5.

Table 5. Comparison of the precisions

Element	Fusion method		Present method	
	Conc. (%)	Av. deviation (%)	Conc. (%)	Av. deviation (%)
Al	0.316	±4	0.316	±5
Fe	0.316	5	0.316	8
Mg	0.316	6	0.316	5
Si	0.316	5	0.316	8

The two methods do not seem to differ significantly in the reproducibilities of their results. Throughout the experiment samples were arced in duplicate with one standard sample in triplicate on each plate.

The accuracy of the present method was studied by comparing with the spectrophotometric determination⁽²⁴⁾ for iron (Table 6).

Table 6. Comparison of the accuracies

Fe added (%)	Spectrochemical			Spectrophotometrical		
	Fe found (%)	Av. deviation* (%)		Fe added (%)	Fe found (%)	Av. deviation* (%)
0.316	0.340	±7		0.316	0.326	±3
0.100	0.092	8		0.100	0.102	2
0.0316	0.030	5		0.0316	0.0312	4

Coloration of crystal; Since the final rutile crystals were slightly yellow in color, a systematic detection of sources of contamination during the crystal growth process was made in each procedure (Table 7). The coloration seems to be due to a relatively large concentration of iron or by an oxygen deficiency in the crystal.

Some contamination of iron and silicon resulted from the calcination procedure. Evidently some of these impurity elements were lost by volatilization and segregation during crystal growth, was carried out at about 1900°C.

* Average of triplicate results.

Table 7. Contamination in each procedure

Procedure	Amount (%)			
	Al	Fe	Mg	Si
Hydrolyzed TiCl ₄ *	0.006	0.010	0.005	0.010
Ammonium titanyle** sulfate	0.006	0.010	0.005	0.010
TiO ₂ powder***	0.003	0.020	0.005	0.020
TiO ₂ crystal****	0.003	0.010	0.001	0.007

Summary

Even though the present technique has some advantages over the conventional method, such as simplicity, rapidity, and greater sensitivity, there are, on the other hand, certain difficulties in interpreting the complex titanium lines which result from the use of the high-temperature source together with the low-energy-level lines already present.

With various doped rutile analysis an average detection limit of approximately 0.006% was readily established for each of the following elements: Co, Cr, Mn, Mo, Nb, Ni, Ta, V, and W.⁽⁶⁾

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Literature Cited

1. A. von Hippel, R. G. Breckenridge F. G. Chesley

* TiCl₄ hydrolyzed with NaOH.

** TiCl₄ solution was added to (NH₄)₂SO₄ solution.

*** (NH₄)₂TiO(SO₄)₂ · 2H₂O was calcined in an electric furnace at 900°C for a hours (a suitable boufe feed for the Verneuil process of growing rutile.

**** Crystal grown with the feed by the flame-fusion technique.

- and L. Tisza, *Ind. Eng. Chem.* **38**, 1097 (1946).
2. E. F. Farrell and A. Linz, *Prog. Rep.*, No. XXX, Lab. Ins. Res., Mass Inst. Tech., January, 1962.
 3. Robert de Lakrue and Frank A. Halden, *Rev. Sci. Instr.* **31**, 35 (1960).
 4. D. C. Cronemeyer, *Phys. Rev.* **37**, 876 (1962).
 5. K. G. Srivastava, *Phys. Rev.* **119**, 516 (1960).
 6. J. Y. Hwang, *Prog. Rep.* No. XXXI, Lab. Ins. Res., Mass. Inst. Tech., July, 1962, p.
 7. C. Feldman, *Anal. Chem.* **21** 1041 (1949).
 8. W. M. Henry.
 9. O. S. Duffendack, K. B. Thomson, W. C. Lee, and O. G. Koppins, *J. Biol. Chem.* **126**, 1 (1938).
 10. M. Fred, N. H. Nachtrieb, and F. S. Tomkins, *J. Opt. Soc. Amer.* **37**, 279 (1947).
 11. J. P. Peterson, *Anal. Chem.* **22**, 1398 (1950).
 12. H. A. Heller and R. W. Lewis, *Anal. Chem.* **25**, 1038 (1953).
 13. H. V. Malmstadt and R. G. Scholtz, *Anal. Chem.* **27**, 881 (1955).
 14. P. R. Perry, R. W. Lewis, and T. A. Sullivan, Bureau of Mines, Report of Investigation, 5168, 1955, p. 23.
 15. N. H. Nachtrieb, D. H. Johnson, and K. S. Dress, *Ind. Eng. Chem., Anal. Ed.*, **15**, 734 (1943).
 16. J. T. Rosza, *The Iron Age* **17**, 166 (1953).
 17. N. I. Tarasevich, K. A. Semenko, and N. F. Meleknina, *Vestn. Moskov Univ., Ser. Khim.* **2**, 64 (1960).
 18. C. W. Nelson, *Prog. Rep.* No. XXX, Lab. Ins. Res., Mass. Inst. Tech., January, 1962, p. 12.
 19. L. H. Ahrens and S. R. Taylor, *Spectrochemical Analysis*, 2nd ed., 1961.
 20. C. E. Moore, *Multiplet Table of Astrophysical Interest*, Princeton Observatory, 1945; C. E. Moore, *Ultraviolet multiplet Table*, U. S. Bureau of Standards, Sec. I, 1950, p. 488.
 21. J. Convey and J. K. Hurwitz, *Research Report No. PM 85*, Canadian Department of Mines and Technical Surveys, 1952.
 22. W. C. Pierce and N. H. Nachtrieb, *J. Opt. Soc. Am.* **13**, 774 (1941).
 23. C. E. Harvey, *Spectrochemical Procedures*, Glendale, Calif., 1950, p. 218.
 24. M. Codell, *Analytical Chemistry of Titanium. Metals and Compounds*, Interscience Publishers, 1959, p. 316.