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MINES BRANCH INVESTIGATION REPORT IR 61-48

**QUANTITATIVE DETERMINATION BY THE
STALLWOOD AIR-JET DC ARC TECHNIQUE.
1. TRACE IMPURITIES IN TITANIUM DIOXIDE**

by

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MINERAL SCIENCES DIVISION

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INTRODUCTION

The use of air-cooled electrodes in the Powder-dc Arc Technique was introduced by B.J. Stallwood in 1951 (1, 2), while working in the Mines Branch. Its quantitative application to steels and ceramics was investigated by R.F. Sturrock and F.A. Lang (3). The work described in this report represents the first of a series of further quantitative applications of the technique.

In the examination of high purity titanium dioxides, no standard samples were available covering the concentration range of impurities present.

To develop a quantitative spectrographic method of analysis for such materials, four samples of high purity TiO_2 were obtained by the courtesy of Ensio,Whiton and Associated of Toronto.

These samples were first analysed by the Mines Branch Stallwood air-jet semi-quantitative dc arc method, and the results of this analysis are shown in Table 1.

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Sample "TQ" was the purest and was chosen as the base material for making known additions of the oxides of the elements appearing as impurities. The resulting master standard was then diluted thrice in succession with further quantities of sample "TQ", and the added amounts of Al, Co, Cu, Fe, Mg, Pb, Sb, Si, W and Zr in the four standards are shown in Table 2.

These standards were then treated by the standard Stallwood procedure, detailed in the Appendix, and working curves prepared from the ratios of line intensities of each impurity element to that of the reference Ti line (Table 3). Correction for the amount of each element present in the base used for the standards was estimated by the procedure described by Duffendack and Wolfe (4). The corrected results are shown in Table 4.

Fifteen spectra of each of the other three samples viz: "AA", "RA" and "TQ 400" were recorded similarly, and the relevant line intensities read, as were the standards, on the Sturrock cathode-ray densitometer.

From these results, the mean concentration of each impurity, and its standard deviation and coefficient of variance were derived, and are shown in Table 5.

The precision of the method varied to some extent from element to element, and ranged from 6% for Al at the 0.17% concentration level to 22% for Cu at the 0.002% level, the mean for all elements being 10% at the 0.01% level.

LITERATURE REFERENCES

- (1) B.J. Stallwood, "Development of a General Method for the Spectrographic Analysis of Powder Samples" Thesis, University of Toronto, (1951).
- (2) B.J. Stallwood, J. Opt. Soc. Am. 44, 171, (1954).
- (3) R.F. Sturrock and F.A. Lang, "Semi-Quantitative and Quantitative Spectrographic Analysis with the Stallwood Air-Jet Source", 1st Ottawa Symposium on Applied Spectroscopy, Mines Branch, Ottawa, September 20, 1954.
- (4) O.S. Duffendack and R.A. Wolfe, Ind. Eng. Chem. Anal. Ed. 10, 161, (1938).

TABLE 1

Semi-Quantitative Analysis

Sample	Per Cent									
	Al	Co	Cu	Fe	Mg	Pb	Sb	Si	W	Zr
AA	0.4	trace	trace	trace	0.06	0.03	1.5	0.2	not detected	0.02
RA	0.3	trace	trace	trace	0.04	0.02	not detected	0.1	"	0.02
TQ	trace	trace	trace	trace	0.04	0.02	"	0.02	"	0.04
TQ 400	0.01	trace	trace	trace	0.03	0.02	"	0.07	2	0.04

TABLE 2

Additions of Elements to Sample "TQ" to form Standards

Standard	Per Cent									
	Al	Co	Cu	Fe	Mg	Pb	Sb	Si	W	Zr
A	1	0.1	0.05	0.1	0.1	0.1	5	0.5	5	0.1
B	0.5	0.05	0.025	0.05	0.05	0.05	2.5	0.25	2.5	0.05
C	0.1	0.01	0.005	0.01	0.01	0.01	0.5	0.05	0.5	0.01
D	0.01	0.001	0.0005	0.001	0.001	0.001	0.05	0.005	0.05	0.001

TABLE 3
Analytical Lines

Element	Wavelength A	Concentration Range, per cent
Titanium	2933.548	Internal Standard
Aluminium	3082.155	0.01 to 1.0
Cobalt	3453.505	0.001 to 0.1
Copper	3247.540	0.0005 to 0.05
Iron	3020.640	0.001 to 0.1
Magnesium	2795.53	0.001 to 0.1
Lead	2833.069	0.001 to 0.1
Antimony	2598.062	0.05 to 5.0
Silicon	2881.578	0.005 to 0.5
Tungsten	2831.378	0.05 to 5.0
Zirconium	3438.230	0.001 to 0.1

TABLE 4

Quantitative Analysis

Sample	Per Cent									
	Al	Co	Cu	Fe	Mg	Pb	Sb	Si	W	Zr
AA	0.30	0.003	0.0009	0.007	0.013	0.010	1.48	0.07	0.52	0.04
RA	0.19	0.007	0.002	0.011	0.006	0.012	not detected	0.04	0.80	0.02
TQ	0.01	0.006	0.003	0.012	0.004	not detected	"	0.005	1.5	0.03
TQ 400	0.01	0.005	0.002	<0.01	0.004	0.011	"	0.014	3.0	0.02

TABLE 5

Precision of dc Arc Method for Impurities in TiO₂

Element	Sample								Average excluding "TQ"	
	AA		RA		TQ		TQ 400			
	%	C.V.	%	C.V.	%	C.V.	%	C.V.		C.V.
Al	0.30	6.9	0.19	7.1	0.01	-	0.01	6.5	0.17	6.8
Co	0.003	11.2	0.007	10.9	0.006	-	0.005	8.2	0.005	10.1
Cu	0.0009	22.5	0.002	17.0	0.003	-	0.002	26.2	0.002	21.9
Fe	0.007	15.8	0.011	14.3	0.012	-	<0.01	-	0.009	10.0
Mg	0.013	7.6	0.006	12.1	0.004	-	0.004	10.2	0.008	10.0
Pb	0.010	10.0	0.012	15.7	<0.003	-	0.011	12.2	0.011	12.6
Sb	1.48	9.6	N.D.	-	N.D.	-	N.D.	-	-	-
Si	0.07	6.0	0.04	12.1	0.005	-	0.014	12.5	0.04	10.2
W	0.52	5.7	0.80	11.6	1.5	-	3.0	9.4	1.5	8.9
Zr	0.04	12.7	0.02	11.5	0.03	-	0.02	22.7	0.03	15.6

C.V. = coefficient of variance

N.D. = not detected

APPENDIX

STALLWOOD SEMI-QUANTITATIVE DC ARC METHOD

Reagents

- (a) National Carbon Co. L 3803 1/8 in. rod drilled to a depth of 1 in. with a 0.086 in. dia. hole (Drill No. 44) and overall length 1 5/8 in.
- (b) National Carbon Co. High Purity Graphite Powder
- (c) Eastman Kodak - S.A. 2 Plates
- (d) Eastman Kodak - Developer D-19
- (e) Eastman Kodak - Fixer F-10

Equipment

Baird 3-metre Grating Spectrograph.
A.R.L. dc Arc Source Unit No. 02825 A.
Sturrock Cathode-Ray Tube Densitometer.
A.R.L. Developing and Fixing Machine.
A.R.L. Plate Dryer.

Exposure

Source	dc Arc
Current	6 amp
Preburn	None
Exposure Period	Complete burning
Upper Electrode	Negative. 1/8 in. dia. pointed rod (National)

Lower Electrode	Positive. Stallwood Pattern (cf "Reagents" above)
Cooling Water	On
Slit	0.025 mm
Sector	1 - 10 - 100% Rotary
Gap	2 mm

Plate Development

Machine rocking at 20°C	
Developer	D-19 for 6 min
Short Stop	Running water for 15 sec
Fixer	F-10 for 10 min
Rinse	Running water for 30 min Sponge off with distilled water.
Drying	Approximately 8 min

Procedure

(a) Weigh 1 mg of finely ground sample and 40 mg of (100 mesh) National Carbon Co. SP-1 graphite powder into a rhodium or platinum plated mixing dish and stir with a graphite rod for one minute.

(b) Transfer to a prepared 1/8 in. dia. graphite electrode by means of a rhodium or platinum plated funnel.

(c) Place electrode in electrode holder box and seal electrode top with a drop of celluloid solution.

(d) Weigh 10 mg of prepared sample and 40 mg of graphite powder and load into electrode similarly.

- (e) Turn on electrode cooling water.
- (f) Place air jet in position and adjust manometer to read 5 in. of water.
- (g) Place sample electrode in lower positive electrode holder and 1/8 in. pointed electrode in upper negative electrode holder.
- (h) By means of the lamp and screen, adjust the gap between the electrodes to 2 mm.
- (i) Ignite the arc by pressing the H.F. igniter button and maintain the gap at 2 mm by continually adjusting the position of the electrodes as seen on the screen. When the sample is completely burned, switch off the arc.

Completion of sample burning is indicated by:-

- (i) the change in colour of the arc and the shape of the electrodes as seen on the screen.
- (ii) an increase in the rate of burning of the electrode and the accompanying change in the noise of the arc.

Complete burning of the sample normally takes from

2 to $2\frac{1}{2}$ minutes.

Photometry

The intensities of the titanium and impurity lines in the standards were read on the Sturrock Cathode-Ray Densitometer and a correction made to the impurity line intensities by subtracting the corresponding intensities found for sample "TQ", which had been used as a base for the standards. The ratios of the corrected impurity line intensities to the titanium internal standard line were plotted against concentration on 5 cycle x 3 cycle log-log graph paper to produce a family of working curves.

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