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## ELECTRON MICROPROBE ANALYSIS OF VANADIUM IN THE PRESENCE OF TITANIUM

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Several writers have drawn attention to the near-coincidence of the  $\text{TiK}_{\beta_{1,3}}$  X-ray emission line ( $\lambda = 2.514 \text{ \AA}$ ) with the  $\text{VK}_{\alpha_{1,2}}$  line ( $\lambda = 2.505 \text{ \AA}$ ). For example, Wright and Lovering (1965), who studied iron-titanium oxides in some New Zealand ironsands, stated that, owing to interference of  $\text{TiK}_{\beta}$ , vanadium analysis with the electron microprobe could not be obtained. Carmichael (1967), in his electron microprobe study of iron-titanium oxides in some salic volcanic rocks, mentioned that the overlap was sufficient to cause difficulty in estimation of vanadium. The experience of these previous workers thus suggested that overlap of radiations would prevent complete analysis of titanium-bearing minerals containing vanadium as a minor constituent, such as is the case with many ilmenites, titanomagnetites and titaniferous chromites.

Recent compositional studies of chromite in chondritic meteorites (Snetsinger *et al.*, 1967; Bunch *et al.*, 1967) revealed the presence of minor amounts of vanadium (between 0.3 and 0.9%  $\text{V}_2\text{O}_3$ ), together with appreciable titanium (average, 2.79%  $\text{TiO}_2$ ). We were particularly concerned with accurate determination of vanadium; therefore a method of eliminating possible  $\text{TiK}_{\beta_{1,3}}$  overlap had to be devised. Use of  $\text{VK}_{\beta_{1,3}}$  as the analytical line was not considered feasible because of the low counting rates which would be involved; in any case there is the question of interference of  $\text{CrK}_{\alpha_{1,2}}$  ( $\lambda = 2.291 \text{ \AA}$ ) with  $\text{VK}_{\beta_{1,3}}$  ( $\lambda = 2.284 \text{ \AA}$ ). Pulse height selection was of no use, because  $\text{VK}_{\alpha_{1,2}}$  and  $\text{TiK}_{\beta_{1,3}}$  radiations are similar in energy. Accordingly, for analysis of vanadium in these chromites, a special method was employed to correct for the interference.

The procedure involved determining the ratio of the intensity of  $\text{TiK}_{\alpha_{1,2}}$  to that of  $\text{TiK}_{\beta_{1,3}}$ , the latter value being measured at the wavelength of  $\text{VK}_{\alpha_{1,2}}$ ; pure rutile ( $\text{TiO}_2$ ) was used for this determination. Then titanium and vanadium were measured on a standard chromite and on the unknown chromite, the  $\text{TiK}_{\alpha_{1,2}}/\text{TiK}_{\beta_{1,3}}$  ratio obtained from rutile being used to correct the  $\text{VK}_{\alpha_{1,2}}$  intensity for interference from  $\text{TiK}_{\beta_{1,3}}$  in the standard and the unknown. Before applying this correction procedure, all intensities were adjusted for drift, background and deadtime. The  $\text{TiK}_{\alpha_{1,2}}$  and  $\text{TiK}_{\beta_{1,3}}$  intensities obtained from rutile were corrected for mass absorption before forming the ratio; in the chromites these values were also corrected for mass absorption and, in addition, for fluorescence of the  $\text{TiK}$

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series by  $\text{FeK}_{\alpha_{1,2}}$  and  $\text{CrK}_{\alpha_{1,2}}$ .<sup>2</sup> The  $\text{VK}_{\alpha_{1,2}}$  intensities in standard and sample chromites were adjusted to take account of mass absorption before subtracting the  $\text{TiK}_{\beta_{1,3}}$  intensities. Corrections for the atomic number effect were negligible, and were not applied. Continuous background was determined by measuring a vanadium- and titanium-free sample (an analyzed olivine) having an average atomic number close to the chromite and rutile, and no interfering lines in the wavelength range of interest. Quite reliable results were obtained; electron microprobe analysis of a titanium-bearing chromite with known vanadium content gave excellent agreement with the wet-chemical value for vanadium. In addition, values for vanadium in two of the meteoritic chromites, obtained with the laser microprobe (Snetsinger and Keil, 1967), agreed closely with values obtained by the above method.

Subsequent further evaluation of this procedure, using a series of analyzed titanium- and vanadium-bearing chromites and a titanioan magnetite, showed, however, that at the titanium and vanadium levels

TABLE 1. COMPARISON OF ANALYSES OF CHROMITE AND MAGNETITE FOR VANADIUM IN THE PRESENCE OF TITANIUM BY WET-CHEMICAL AND ELECTRON MICROPROBE TECHNIQUES (WEIGHT PERCENTS)<sup>a</sup>

Wet-Chemical Analyses			$\text{V}_2\text{O}_5$ ; Electron Microprobe Values	
Sample	$\text{TiO}_2$	$\text{V}_2\text{O}_5$	Corrected value using described method	Corrected for continuous background only
G-4	0.92	0.17	0.20	0.21
G-23AB	0.76	0.19	0.12	0.12
IM-13	1.00	0.55	0.50	0.51
MV-54A	0.70	0.19	0.22	0.22
G-17	0.82	0.20	0.20	0.20
9506	6.92	0.22	0.23	0.24

<sup>a</sup> All sample are chromite, with the exception of 9506, a titanioan magnetite.

in question, interference is negligible, and application of the proposed correction procedure is actually unnecessary. Comparison of the last two columns in Table 1, where values corrected for overlap using the above method are listed with results corrected only for continuous background, reveals agreement, suggesting that at these titanium and vanadium levels interference of  $\text{TiK}_{\beta_{1,3}}$  with  $\text{VK}_{\alpha_{1,2}}$  is insignificant.

In order to determine possible overlap at higher titanium levels, recourse was made to N.B.S. Standard Reference Materials 654, 653 and 173a, as an analyzed ilmenite was not available. The standards are ti-

<sup>2</sup> Philibert's (1963) equation, as modified by Duncumb and Shields (1966), and Heinrich's (1966) mass absorption coefficients were used in calculating the mass absorption corrections. The method used to estimate fluorescence corrections was taken from an unpublished 1962 report by D. B. Wittry, Univ. S. Calif. Eng. Center.

tanium-base alloys containing vanadium and aluminum. For these experiments pure vanadium was used as a standard for vanadium, and the  $\text{TiK}_{\alpha_{1,2}}/\text{TiK}_{\beta_{1,3}}$  ratio was obtained from pure titanium. Pure chromium, similar in atomic number to all the standards, was used to measure continuous backgrounds. The correction procedure was carried out in analogy to the chromite data, and all instrumental and matrix-effect corrections were made. The ones for atomic number and fluorescence were, however, negligible. Results of the experiments are given in Table 2. Values in the last column are slightly higher than the standardized wet-chemical vanadium values (column 3), and this is a result of overlap of  $\text{TiK}_{\beta_{1,3}}$  with  $\text{VK}_{\alpha_{1,2}}$  at these higher titanium levels. Using the procedure

TABLE 2. COMPARISON OF ANALYSES OF TITANIUM-BASE ALLOYS FOR VANADIUM IN THE PRESENCE OF TITANIUM BY WET-CHEMICAL AND ELECTRON MICROPROBE TECHNIQUES (WEIGHT PERCENTS)

Wet-Chemical Analyses			Vanadium; Microprobe Values	
Standard	Ti	V <sup>a</sup>	Corrected value using described method	Corrected for continuous background only
654	90.14	3.83	3.73	4.08
653	90.17	2.58	2.46	2.81
173a	89.23	4.06	3.92	4.26

<sup>a</sup> The remainder of each standard is aluminum.

described above to correct for overlap, closer agreement with the wet-chemical values is obtained (column 4). Assuming that the wet-chemical determinations are accurate, the data corrected according to the procedure described above are about a tenth of a percent lower, and despite careful consideration of all factors involved, we are unable to explain this. The main point of the data is, however, that, even in these extreme cases of high titanium, interference with vanadium is minimal: vanadium values uncorrected for overlap are only about 0.2 percent higher than the wet-chemical determinations. This suggests that with a terrestrial ilmenite containing 32 percent titanium and, for example, one percent vanadium, the vanadium value would be approximately 0.06 percent too high—a negligible excess in most practical analytical situations.

It is emphasized that the experimental conditions employed here were in no way unusual. An ARL-EMX probe was used, with a LiF crystal mounted on a 4 inch Rowland circle, and a sealed argon proportional counter. The secondary slits were open to 0.015 inch, a routine setting with these instruments.

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## PREPARATION OF THIN FILM SECTIONS

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A new technique has been developed for the preparation of petrographic (rock, mineral, and coal) thin film sections. In this technique the section is freed from the glass slide and coated with soluble transparent plastic, to give a coherent, flexible specimen which may be handled without risk of breakage.

Uses of such specially prepared thin film sections include: specimens for chemical analysis of small portions of a rock or of a single mineral grain (for example, where compositional zoning is suspected) material for heating-stage studies; starting material for preparation of ultrathin sections for electron microscopy by chemical thinning; and for mounting to make slides for projection.