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DETERMINATION OF TOTAL IRON IN HEMATITIC IRON ORES BY X-RAY FLUORESCENCE SPECTROMETRY

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Abstract.—A suite of hematitic iron-ore samples was analyzed by X-ray fluorescence spectrometry. Computations were made to derive an empirical equation from which the amount of iron in a sample can be calculated. The changes from true values caused by interfering elements are compensated for by simple calculation. Comparisons with wet chemical analyses are shown

A suite of iron-ore samples was analyzed to check the reliability of a field method (Sheldon, 1964) for estimating iron content of hematitic iron ores. X-ray fluorescence spectrometry was selected because of its relative simplicity, rapidity, reasonable accuracy, and the wide range of elements that can be analyzed without much additional work on the samples. It was found that analyses for iron obtained by X-ray spectrometry were comparable in accuracy to the classical volumetric methods.

The X-ray spectrometric analyses were made using a Norelco 50 KV-50MA X-ray spectrometer with helium-path attachment and an FA-60 X-ray tube with molybdenum target. A lithium fluoride analyzing crystal, a primary collimator tube $\frac{3}{4}$ inch square by 4 inches long, and a secondary collimator 4 inches long with 0.005-inch Soller slits were used exclusively. A flow proportional counter using P-10 gas and operated at 1,550 volts was used as a detector.

All samples were crushed to $\frac{1}{4}$ -inch fragments or smaller in a small jaw crusher and then were ground to 80-100 mesh with a mechanical grinder fitted with ceramic plates. A chart scan of each sample, before preparation, was made at the rate of 1° of arc per minute in order to estimate roughly the concentration of elements that might interfere with the iron determination through absorption effects. These estimates were made by comparison with an appropriate standard made up with an SiO_2 matrix.

In these iron-ore samples, calcium and silicon were the only interfering elements present in appreciable

quantities. None of the samples contained more than 25 percent calcium. All samples were prepared as follows: Enough CaCO_3 was added to a 0.1500-g sample to make the total calcium equal to approximately 25 percent of the sample by weight (0.0375 g calcium). SiO_2 was added to bring the total weight of the mixture of sample, CaCO_3 and SiO_2 , to 0.3000 g. Boric acid as a noninterfering diluent was then added to obtain a total weight of 1.500 g. Each sample mixture was ground to an impalpable powder in an agate pestle and mortar under acetone, allowed to dry while grinding, and then pressed at 30,000 lbs. for 10 seconds into a pellet with a base of boric acid.

Although the presence of silicon reduced the intensity of the Fe peak, SiO_2 was made the predominant matrix component in the prepared sample. The Fe standards were made up as Fe_2O_3 in SiO_2 . The effect of the small differences between the amounts of SiO_2 in the samples and the amount in the standards was negligible because of the predominance of SiO_2 as a matrix component. However, one must correct for absorption due to calcium and silicon.

Lachances' (written communication, 1960) correction factors, equations 1 and 2, and his expression for the iron content, equation 3, were modified as follows:

$$F_{\text{Ca}} = \frac{A - B_{\text{Ca}}}{B_{\text{Ca}} \times \text{percent Ca}} \quad (1)$$

$$F_{\text{Si}} = \frac{A - B_{\text{Si}}}{B_{\text{Si}} \times \text{percent Si}} \quad (2)$$

$$\text{Percent Fe} = B' + (B_{\text{Ca}} \times F_{\text{Ca}} \times \text{percent Ca}) + (B'_{\text{Si}} \times F_{\text{Si}} \times \text{percent Si}), \quad (3)$$

where F_{Ca} = factor for absorption due to Ca,
 F_{Si} = factor for absorption due to Si,
 A = actual percentage of Fe in standard,

- B = apparent percentage of Fe in same standard with matrix added,
- B_{Ca} = apparent percentage of Fe in same standard with Ca added,
- B_{Si} = apparent percentage of Fe in same standard with Si added,
- B' = apparent percentage of Fe in sample, effected by matrix,
- B'_{Ca} = apparent percentage of Fe in sample, effected by Ca, and
- B'_{Si} = apparent percentage of Fe in sample, effected by Si.

By substituting equations 1 and 2 in 3, there is obtained

$$\text{Percent Fe} = \frac{B' + (B_{Ca} \times [A - B_{Ca}] \times \text{percent Ca})}{B_{Ca} \times \text{percent Ca}} + \frac{(B'_{Si} \times [A - B_{Si}] \times \text{percent Si})}{B_{Si} \times \text{percent Si}}$$

and upon simplification this equation becomes

$$\text{Percent Fe} = \frac{B' + (B'_{Ca} \times [A - B_{Ca}])}{B_{Ca}} + \frac{(B'_{Si} \times [A - B_{Si}])}{B_{Si}}$$

Since the effect of the matrix is equal to the sum of the effects of each component in the matrix, this equation can be rewritten into the following form:

$$\text{Percent Fe} = \frac{B' + (B' \times [A - B])}{B} = B' \frac{(1 + [A - B])}{B}$$

The factor $\frac{A - B}{B}$ is practically constant for all percentages of iron sought, and it is constant regardless of instrumental variations caused by normal fluctuations of voltage and temperature from day to day.

Although this suite of iron-ore samples has a comparatively simple matrix composition, the method of computation has been used in analyzing samples containing as many as five interfering elements. The method has the advantage of allowing use of the same set of standards for rock and ores of widely varying matrices.

Tables 158.1 and 158.2 show the accuracy and reproducibility of analytical results obtained by X-ray emission spectrometry of hematitic iron ores. The accuracy is based on the assumption that the chemical

results are the absolute values. The chemical analyses were made by the standard dichromate volumetric oxidation-reduction method. Only one determination was made on each sample by each method. X-ray results are given to hundredths of a percent for comparison but should not be considered accurate beyond two figures. The reproducibility of results of the method was determined by analyzing each of the 10 samples 3 times.

TABLE 158.1.—Comparison of results obtained by chemical and X-ray spectrographic methods

Sample No.	(1)	(2)	(3)	(4)
	Fe (percent) by X-ray method	Fe (percent) by wet chemical method ¹	Absolute difference (1)-(2)	Absolute percentage variation 100 (3)/(2)
J12-13-----	2.70	2.65	0.05	1.89
J12-8-----	5.25	5.27	.02	.38
J12-20b-----	10.86	10.86	.00	.00
J3-30-1-----	15.74	15.79	.05	.32
J3-30-3-----	18.15	18.23	.08	.44
J12-28b-----	21.47	21.65	.18	.83
J3-33b-----	26.93	26.80	.13	.49
J12-40h-----	31.59	31.50	.09	.29
J3-32f-----	34.93	34.26	.67	1.96
J3-32i-----	44.11	44.78	.67	1.50
Average-----				.81

¹ Analyst: Dwight L. Skinner, chemist, U.S. Geological Survey, Denver, Colo.

TABLE 158.2.—Reproducibility of analytical results for iron by X-ray emission spectrography

Sample No.	(1)	(2)	(3)	(4)	(5)	(6)
	Fe (percent) 1st run	Fe (percent) 2d run	Fe (percent) 3d run	Average	Absolute mean deviation $\frac{ (4)-(1) + (4)-(2) + (4)-(3) }{3}$	Absolute percentage variation (5)/(4)
J12-13-----	2.70	2.69	2.62	2.67	0.03	1.12
J12-8-----	5.25	5.44	5.37	5.35	.07	1.31
J12-20b-----	10.86	10.91	11.02	10.93	.06	.55
J3-30-1-----	15.74	15.31	15.72	15.59	.19	1.22
J3-30-3-----	18.15	19.07	19.17	18.80	.43	2.29
J12-28b-----	21.47	22.78	22.66	22.30	.56	2.51
J3-33b-----	26.93	27.00	27.23	27.05	.12	.44
J12-40h-----	31.59	31.86	32.04	31.83	.16	.50
J3-32f-----	34.93	35.16	34.35	34.61	.38	1.10
J3-32i-----	44.11	43.49	44.09	43.90	.27	.62
Average-----						1.17

REFERENCE

Sheldon, R. P., 1964, Relation between specific gravity and iron content of rocks from the Red Mountain Formation, Alabama: U.S. Geol. Survey Bull. 1182-D. [In press]

