

SEQUENTIAL DETERMINATION OF IRON AND TITANIUM BY FLOW-INJECTION ANALYSIS

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Summary—A flow-injection method has been developed for the sequential spectrophotometric determination of iron and titanium using 3,4 dihydroxybenzoic acid as chromogenic reagent. The system involves the sequential measurement of the absorbances of the complexes at 380 and 570 nm. The system is designed using a simultaneous injection of sample and reagent into separate carrier streams. The proposed method is characterized by a precision of about 2%, a sampling rate of about 50 samples per hour, and a reagent consumption of 200 μ l (0.50% solution) per sample. It is relatively free of interferences and was used for the sequential determination of titanium and iron in rocks.

Flow-injection analysis (FIA) is a rapid and precise technique which has found wide application, especially in agricultural, environmental, geochemical, clinical and pharmaceutical analysis. The reaction between 3,4 dihydroxybenzoic acid (protocatechuic acid) or DHB with iron(III) and titanium(IV) allows the sequential determination of iron and titanium by flow injection, based on the additive property of the absorbances. Iron(III) reacts with this reagent, forming a complex with absorption maxima at 380 and 570 nm, and titanium(IV) forms a complex with an absorption peak at 380 nm. Considering these facts, a method is proposed in which the absorbances are measured at 380 and 570 nm. DHB is a good reagent for flow-injection analysis, because it is soluble in water (2 g/100 ml)¹ and does not absorb in the visible region of the spectrum. The reaction of iron(III) with DHB was studied by Hsieh and Liang² and of titanium(IV) with DHB by Sommer.³ The 3,4 dihydroxybenzoic acid reagent has been used in the flow-injection analysis of manganese^{4–6} and for conventional spectrophotometric determination of molybdenum,⁷ vanadium,^{8,9} cerium¹⁰ and niobium.¹¹

EXPERIMENTAL

Reagents

3,4 Dihydroxybenzoic acid solution. A 2.5-g amount was dissolved in 500 ml of water.

Standard iron(III) solution. Prepared from iron(III) sulfate heptahydrate and standardized gravimetrically.

Standard titanium(IV) solution.¹² Prepared by dissolving titanium(IV) oxide (0.20 g) in sulphuric acid (8 ml) and ammonium sulfate (3.2 g), heating and dilution with distilled water.

Buffer solution (pH 6.0). Prepared by dissolving 0.31 ml of acetic acid and 12.88 g of sodium acetate trihydrate in one litre of distilled water.

Apparatus

A Varian DMS 100 spectrophotometer equipped with an 8- μ l flow cell, a Fisher 600 pH meter, a Micronal B332 peristaltic pump and an Intralab recorder were used.

Sample preparation

Weigh 0.2–0.3 g of dry material (110°), transfer to a Teflon beaker, and add a few milliliters of water so as to form a wet mixture. Add 1 ml of sulphuric acid (98%) and 10 ml of hydrofluoric acid (40%). Heat, on a hot plate, until almost dry.

Add an additional 1 ml of sulphuric acid and 10 ml of hydrofluoric acid and heat until white fumes. Add 5–10 ml of hydrochloric acid (37%) and transfer the contents of the beaker to a 250-ml glass beaker.

Boil to dissolve completely all the residue, cool to room temperature and transfer, with demineralized water, to a standard flask and dilute to volume.

Flow-injection analysis

Carrier solution C (buffer solution pH 6.0) is pumped into the analytical lines at a flow-rate of 3.50 ml/min with a peristaltic pump

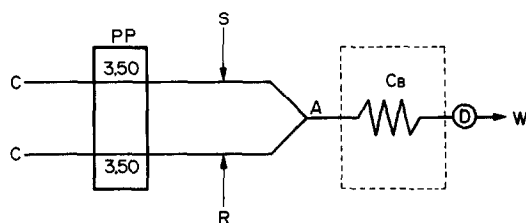


Fig. 1. Flow diagram: C carrier solution (buffer solution pH 6.0), PP peristaltic pump, S sample, R chromogenic reagent solution, A confluence point, C_B mixing coil (0.5 mm i.d., 100 cm long), D detector—equipped with flow cell (volume 8 μ l), W waste.

[Fig. 1]. The sample solution *S* (200 μ l) and reagent solution *R* (200 μ l) are introduced simultaneously into the carrier streams by a double proportional injector and the absorbance of the complex is monitored in the flow-through cell *D* at 380 nm for the titanium(IV)-complex and 380 and 570 nm for the iron(III)-complex, against the carrier solution as reference (baseline), separate injections are made for measurements at the two wavelengths. A narrow coil (100 cm long) is attached before the flow-through cell, as a back-pressure and mixing coil.

For calibration, similarly treated standard solutions are injected between the sample runs. The area or height of the absorbance peak can be used for calibration.

RESULTS AND DISCUSSION

The iron(III) reacts with DHB in the range pH 5.0–6.0 forming a complex with absorption maxima at 380 and 570 nm and molar absorptivities of 2.84×10^3 and 4.10×10^3 l·mole⁻¹·cm⁻¹, respectively. The titanium forms a complex with DHB in the pH range 4.0–6.0, with an absorption maximum at 380 and a molar absorptivity of 1.54×10^4 l·mole⁻¹·cm⁻¹ (Fig. 2). The DHB has an absorption peak at 280 nm and does not absorb in the visible spectrum. Considering these facts, the present method is proposed by measuring the absorbances at 380 and 570 nm, based on the additive property of the absorbances.

Optimization of flow system

Buffer concentration. The effect of the concentration of buffer solution was investigated from 0.100 to 1.000M acetate. Increasing the buffer to high concentrations increases the sensitivity but decreases the reproducibility. Concentrations below 0.100M are not recommended because the “buffering capacity” is low and the sample solutions are acid. The proposed system utilizes a dilute acetate solution, 0.100M, as the carrier stream.

Effect of pH. The effect of pH was investigated by using acetate buffer (0.100M) of various pH values as the carrier stream. Maximum absorbance is found between pH 5.5 and 6.0.

Flow rate. The effect of the flow-rate on the peak height was studied in the range of 2–4.5 ml/min, by injecting 200 μ l each of iron standard and reagent solution. The maximum signal was obtained with a flow-rate of 3.50 ml/min for each stream.

Reagent and sample volume. The influence of the sample volume on the absorbance was investigated by injecting different volumes (50–300 μ l) of iron and titanium standard solutions into the carrier stream at the recommended flow-rate and coil length, keeping the reagent volume at 200 μ l. The injection volume has a significant effect, yielding increased peak height and reproducibility with increasing injection volume. However, increasing the injection volume widens the sample zone and lowers the sampling rate, so that 200 μ l is taken as a compromise.

Length of coil. The effect of the length of the reaction coil was examined for various flow-rates. Coil lengths of 50, 100 and 150 cm were tested. Increasing the coil length lowered the peak height but improved the reproducibility. The optimum length was established as 100 cm.

Reagent concentration. The influence of the 3,4-dihydroxybenzoic acid concentration, ranging from 0.10 to 1.00%, was tested, using 200 μ l of reagent and of sample. A calibration graph was obtained for each concentration of reagent with iron and titanium standards,

Table 1. Sequential determination of iron and titanium in synthetic samples

Proportion iron:titanium	Titanium (μ g/ml)		Iron (μ g/ml)	
	present	found*	present	found*
1.1	11.06	10.68 \pm 0.10	11.27	10.91 \pm 0.10
2.8	8.05	8.33 \pm 0.12	22.55	22.23 \pm 0.12
4.5	8.05	8.12 \pm 0.15	36.08	35.91 \pm 0.15
9.0	4.02	4.09 \pm 0.10	36.08	36.14 \pm 0.11

*95% Confidence level.

Table 2. Sequential determination of iron and titanium in geological matrices

Standards rocks	Titanium (TiO ₂) (%)		Iron (Fe ₂ O ₃) (%)	
	certified	found*	certified	found*
Bauxite NBS-USA	2.78	2.86 ± 0.10	5.82	5.79 ± 0.15
Clay 1—IPT-SP	0.24	0.2 ± 0.07	1.93	1.88 ± 0.10
Clay 2—IPT-SP	1.04	0.96 ± 0.11	1.28	1.28 ± 0.09
Granite-CEPED-Ba	0.26	0.29 ± 0.09	1.62	1.63 ± 0.11
Bauxite-CEPED-Ba	1.19	1.24 ± 0.12	9.44	9.61 ± 0.13

*95% Confidence level.

Table 3. Compositions of standards analyzed

Standards	Al ₂ O ₃ (%)	SiO ₂ (%)	CaO (%)	MgO (%)	Na ₂ O (%)	K ₂ O (%)
Bauxite NBS-USA*	55.00	6.01	0.29	0.02	0.02	0.01
Clay 1—IPT-SP†	38.40	45.10	0.07	0.14	0.01	0.85
Clay 2—IPT-SP*	29.10	55.80	0.09	0.20	0.01	0.29
Granite-CEPED-BA*	15.06	71.80	1.21	0.50	3.79	4.78
Bauxite-CEPED-Ba*	61.47	—	0.04	0.05	0.06	0.03

*Source of the certified sample.

ranging from 10.0 to 30.0 µg/ml; all measurements were performed in triplicate. The maximum and constant slope of the calibration curve was obtained above 0.40% reagent concentration, so 0.50% concentration was selected as optimal. A study was made with 200 µl of the reagent solution.

Calibration graph

A calibration graph was obtained at the optimum working conditions: reaction coil = 100 cm, flow-rates 3.50 ml/min, reagent concentration = 0.50%, volume injected = 200 µl and carrier stream = acetate buffer pH 6.0. The calibration graph was linear over the range 2–10 µg/ml for titanium and 10–40 µg/ml for iron.

Effect of foreign ions

The interference due to several anions and cations was studied in detail. In the flow-injection spectrophotometric determination of 2 ppm of iron(III) and 1 ppm of titanium(IV), V(V), Mo(VI), Ce(III), Nb(V), phosphate and tartrate ions interfered seriously. The following ions [when present in the amounts (in ppm) shown in brackets] do not interfere: Mn²⁺ (20), Hg²⁺ (4), Cu²⁺ (10), Co²⁺ (40), Al³⁺ (50), Ni²⁺ (60), Ca²⁺ (75), Mg²⁺ (75), Pb²⁺ (40), La³⁺ (40), Bi³⁺ (40), Sr²⁺ (40), SO₄²⁻ (200), CO₃²⁻ (40), Cl⁻ (200) and NO₃⁻ (200).

However, the proposed method can be conveniently applied for the simultaneous determination of iron(III) and titanium(IV) in silicate rocks that do not contain interferents such as vanadium(V), molybdenum(IV),

cerium(III) and niobium(V), as illustrated below.

Determination of iron and titanium in synthetic samples and standard samples of rocks by flow-injection analysis

The flow-system proposed was used for the simultaneous determination of iron and titanium in several samples. The results in Table 1 show that the method can be used for determination of iron and titanium in several proportions.

The analysis of rocks revealed (Table 2) that the proposed method has satisfactory precision and can be used for determination

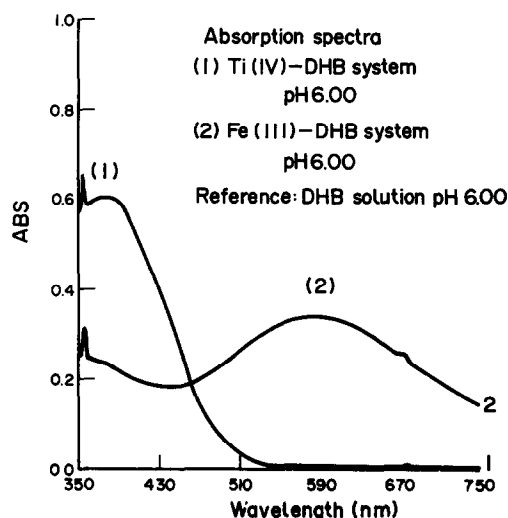


Fig. 2 Absorption spectra (1) T_i(IV)-DBH system pH 6.00 (2) Fe(III)-DHB system pH 6.00 reference: DHB solution pH 6.00.

of iron and titanium in rock samples with different composition (Table 3).

DHB does not show as high a sensitivity for iron as other reagents do but it is good for titanium. However, this presents a favorable situation for the sequential determination of these elements because, in large numbers of samples, the iron level is superior to that of titanium.

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