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USE OF 1-(2-THIAZOLYLAZO) 2-NAPHTHOL IN RAPID DETERMINATION OF IRON IN GEOLOGICAL MATRICES

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Summary—The present work describes the use of 1-(2-thiazolylazo)-2-naphthol (TAN) as a spectrophotomeric reagent for iron determination. TAN reacts with iron(II) forming a brown complex with absorption maximum at 575 and 787 nm. The following parameters were studied: complex stability, pH effect, amount of the TAN, buffer selection, amount of acetate buffer, reductor effect, order of addition of reagents and adherence to Beer's Law. The results demonstrated that iron can be determined with TAN in a pH range of 4.0–6.2 with an apparent molar absorptivity of 1.83×10^4 l . mol^{-1} . cm^{-1} (at 787 nm) and 1.41×10^4 l . mol^{-1} . cm^{-1} (at 575 nm). Beer's Law is obeyed for at least 3.00 μg/ml. The TAN reacts with other cations, but at 787 nm only the iron(II)–TAN complex absorbs. So, iron can be determined selectively in the presence of several cations. A procedure based on the direct mixture of the sample and a chromogenic solution is proposed, where iron can be determined rapidly and easily. Such procedures were used for the determination of iron in several geological matrices. No significant differences were obtained for TAN method and certificate results.

Iron is one of the main constituents of geological matrices and its determination in geological laboratories is always routine. Flame AAS and ICP-OES have been frequently used. Generally[1] lower detection limits and enhanced selectivity of atomic spectrometric techniques, together with the ease of sequential multielement determination capabilities, make these techniques better suited for metals determination in gelogical matrices than spectrophotometry. Spectrophotometry, however, continues to enjoy wide popularity. The common availability of the instrumentation and the simplicity of procedures as well as speed, precision, and accuracy of the technique still make photometric methods an attractive alternative, resulting in an extensive literature being published. In spectrophotometry, the matrix effect is relatively smaller than flame AAS and ICP-OES.

In the present paper, a rapid and accurate method for iron determination in geological matrices is proposed, using 1-(2-thiazolylazo)-2-naphthol (TAN) as the spectrophotometric reagent. A derivative procedure allows iron determination in freshwater.

1-(2-thiazolylazo)-2-naphthol (TAN) forms several coloured complex with many cations, and has been used for spectrophotometric determination of zinc,[2] nickel,[3] vanadium,[4] cobalt,[5] thallium[6] and others.[7] However, its potential as spectrophotometric reagent for iron has not been explored.

EXPERIMENTAL

Reagents

All reagents were of analytical reagent grade unless otherwise stated.

Iron(III) solution (1000 μg/ml). Prepared by dissolving pure iron (99.99%) in diluted hydrochloric acid and dissolution up to 1 l. with demineralized water.

Triton X-100 solution (10%). Prepared by dissolving of 25.0 g (Merck) up to 250 ml with demineralized water.

TAN solution ($4 \times 10^{-3}M$). Prepared by dissolving 0.25 g (Merck) in 25 ml ethyl alcohol and dilution up to 250 ml with Triton X-100 solution (10%).

Buffer solution (pH 4.75). Prepared by mixing 68.0 g of trihydrate sodium acetate and 29.4 ml of glacial acetic acid in 1 l. of demineralized water.

Reductor solution (10%). Prepared by dissolving of 10.0 g of hydroxylammonium chloride in 100 ml of demineralized water.

Chromogenic solution. Prepared by mixing 200 ml of buffer solution with 40 ml of reducter solution, 40 ml of TAN solution and dissolution up to 500 ml with demineralized water.

Apparatus

Absorption spectra, first-derivative spectra and absorbances were recorded and measured with a Varian DMS-80 spectrophotometer and an Intralab recorder using 1.0-cm cells.

A 300 Analyser pH meter was used to measure the pH values.

General procedure

Spectrophotometric determination of iron (Procedure A). A portion of solution containing 25.00 μg of iron(III) was transferred to a 25 ml standard flask. 1.0 ml of reductor solution (10%) and 5.0 ml of acetate buffer (pH 4.75) added, mixed and 1.0 ml of TAN ($4 \times 10^{-3}M$) solution added. It was diluted to the mark with water and the absorbance at 787 nm measured in a 1-cm cell, using an appropriate blank.

Rapid spectrophotometric determination of iron (Procedure B). An aliquot of the 10.0 ml sample solution was transferred to a completely dry flask and 10.0 ml of the chromogenic solution added (described above), it was mixed thoroughly and the absorbance at 787 nm measured in a 1-cm cell, using an appropriate blank.

First-derivative spectrophotometry (Procedure C). A portion of solution containing 4.00 μg of iron(III) was transferred to a 25 ml standard flask. 1.0 ml of reductor solution (10%) and 2.5 ml of acetate buffer (pH 4.75) added, mixed and 1.0 ml of TAN ($4 \times 10^{-3}M$) solution added. It was diluted to the mark with water, mixed and the first-derivative spectrum from 900 to 600 nm recorded against an appropriate blank, at a scan speed of 100 nm min and slit of 4 nm.

The first-derivative signal amplitude (H) was measured with the recorder voltage 2 or 5 mV.

RESULTS AND DISCUSSION

Characteristics of the reagent and the complex

The reaction of TAN with iron(II) cation in the presence of Triton-X100 forms a brown complex with absorption maxima at 575 and 787 nm and composition of 1:2 iron–TAN. The complex is instantaneously formed and stable for at least 2 hr. The TAN reagent has an absorption maximum at 487 nm (at pH 4.75). It and its iron(II) complex have a low solubility in water but the reaction in the presence of Triton-X100 solves this inconvenience.

Affect of pH

The affect of pH on the iron(II)–TAN system was studied and the results demonstrated that the absorbance signal is maximum and constant in a pH range 4.0–6.2 (Fig. 1). The general procedure was developed with an acetate buffer at pH 4.75, because in this pH the buffer-index of the acetate buffer is maximum, and the TAN selectivity is higher.

Affect of the amount of acetate buffer solution

The affect of the buffer concentration on the iron(II)–TAN complex was studied and the results demonstrated that it does not affect the absorbance signal of the system when the buffer is in the concentration range of 0.1–0.6M acetate (Table 1).

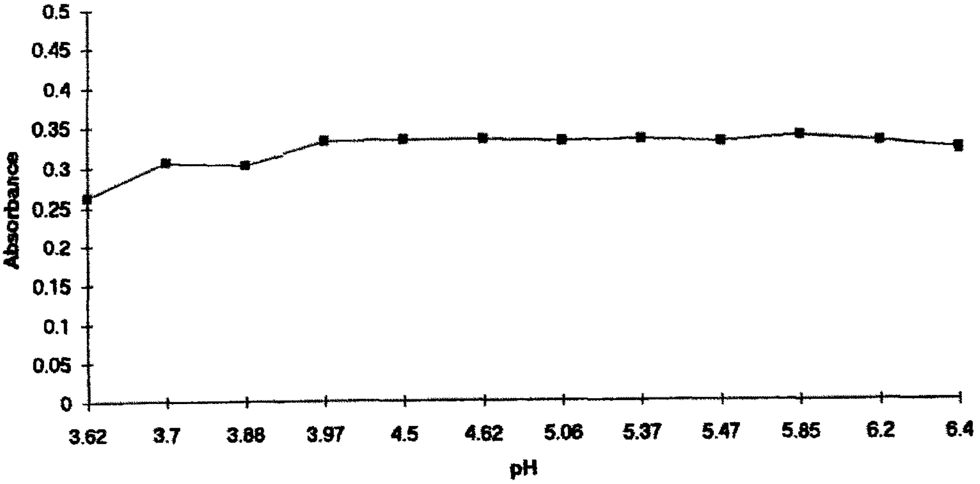

Fig. 1. Effect of pH on the Fe–TAN system.

Table 1. Affect of the amount of acetate buffer solution

Acetate buffer concentration (M)	Absorbance
0.1	0.331
0.2	0.336
0.3	0.332
0.4	0.335
0.5	0.328
0.6	0.333

Affect of the order of addition of reagents on the complex formation

The addition order of the reagents was studied and the results demonstrated that it does not affect the complex formation, although the chromogenic system involves a reaction of reduction of iron(III) to iron(II) using the hydroxylamine hydrochloride as reductor agent (Table 2).

Amount of TAN for complex formation

A maximal and constant absorbance signal was obtained for 25.00 μg of iron with 250 μl of TAN ($4 \times 10^{-3}M$) solution per 25 ml. Thus, 1.0 ml of solution was selected as optimal for general procedure.

Conditions for the measurement of first-derivative value

Effects of the scan speed and of the slit width (Δl) were examined on the measurement of first-derivative signal. The results showed that scan speed did not affect the value. In this way, the scan speed of 100 nm/min was chosen. It was also found that there was no significant difference in sensitivity among various Δls, but an increase of slit width decreased the noise, hence a slit of 4 nm was selected for the measurements. The decrease of recorder voltage obviously does increase the first-derivative signal but also increases the noise.

The method used for the quantitative evaluation of derivative spectra signal is classified as the 'peak-zero method'.[8]

Table 2. Affect of the order of addition

Order of addition	Absorbance
Fe(III) + reductor + buffer + TAN	0.330
Fe(III) + reductor + TAN + buffer	0.325
Fe(III) + buffer + TAN + reductor	0.330
Fe(III) + buffer + reductor + TAN	0.332
Fe(III) + TAN + reductor + buffer	0.329
Fe(III) + TAN + buffer + reductor	0.329

Table 3. Iron determination in the presence of various ions

Ion	100 × 1	10 × 1	1 × 1	Reagent used
Ca(II)	N	N	N	$CaCO_3$/HCl
Mg(II)	N	N	N	$MgCl_2 . 6H_2O$
Ba(II)	N	N	N	$BaCl_2 . 2H_2O$
Sr(II)	N	N	N	$Sr(NO_3)_2$
Al(III)	N	N	N	$Al_2(SO_4)_3$
Mn(II)	N	N	N	$MnSO_4 . 6H_2O$
Bi(III)	N	N	N	$Bi(NO_3) . 5H_2O$/HCl
Cd(II)	I	N	N	Cd(Ac) . $2H_2O$
Pb(II)	I	N	N	$Pb(NO_3)_2$
In(III)	I	N	N	In_2O_3/HCl
Zn(II)	I	N	N	$ZnSO_4 . 7H_2O$
Cu(II)*	I	I	N	$CuSO_4 . 5H_2O$
Ni(II)	I	I	N	$NiSO_4 . 7H_2O$
Ti(IV)	I	I	N	TiO_2/H_2SO_4
Hg(II)*	I	I	N	HgO/HNO_3
Co(II)	I	I	I	$CoSO_4 . 7H_2O$
Cl(I)	N	N	N	NaCl
SO_4(II)	N	N	N	Na_2SO_4
CO_3(II)	N	N	N	Na_2CO_3
NO_3(I)	N	N	N	$NaNO_3$
PO_4(III)	I	N	N	Na_3PO_4

I = interferes, N = does not interfere.
*Can be masked with thiosulphate.

Affect of interfering ions

Solutions containing 10.00 μg of iron(III) and various proportions of several cations and anions were prepared and procedure A was followed. The interference limit of an ion was determined as the proportion in which a change of $\pm 2\%$ in absorbances of the chelates were observed (Table 3). The effect of ionic strength on the system was negligible for $0.1M$ concentrations of sodium chloride and potassium nitrate.

Analytical characteristics of the method

In the conventional photometric method, Beer's Law was obeyed in the iron concentration range 0–3.0 μg/ml, and the graph passed through the origin. The molar absorptivities were 1.83×10^4 $l.mol^{-1} . cm^{-1}$ at 787 nm and 1.41×10^4 $l.mol^{-1} . cm^{-1}$ at 575 nm. The calibration graph for the derivative method was linear for 0–400 ng/ml iron concentration. The calibration curves were described in procedures A–C in the experimental part. The analytical sensitivity,[9] calibration sensitivity,[9] the limit of detection and the limit of quantitation[10] as well as other analytical characteristics of the procedures A and B are summarized in Table 4.

Application

Procedures A and B were applied to iron determination in clay, andesite, bauxite, basalt, granite, rhyolite, bentonite and manganese ore.

Table 4. Analytical characteristics of the procedures

	Ordinary spectrophtometric	First-derivative spectrophotometric
Calibration sensitivity	0.322 ml/μg	26.68 ml/μg
Analytical sensitivity	78.0 ml/μg	256.8 cm . ml/μg
Limit of detection (C_L)	24 ng/ml	7.5 ng/ml
Limit of quantification (C_Q)	80 ng/ml	25.1 ng/ml
Linear dynamic range	0.08–3.00 μg/ml	0.02–0.40 μg/ml
Coefficient of variation	1.25%	1.67%

Table 5. Iron determination in standards (% Fe_2O_3)

Standards	Conventional method (%)*	Practical method (%)*	Value certified (%)
Andesite GSJ JA-1	6.96 ± 0.11 (4)	7.03 ± 0.09 (7)	6.95
Basalt GSJ JB-1a	8.95 ± 0.08 (3)	9.08 ± 0.07 (5)	9.10
Rhyolite GSJ JR-1	0.94 ± 0.02 (6)	0.95 ± 0.01 (5)	0.96
Rhyolite GSJ JR-2	0.84 ± 0.01 (5)	0.83 ± 0.01 (6)	0.86
Bauxite NIST 69A	5.80 ± 0.13 (4)	5.87 ± 0.09 (5)	5.82
Basalt UFBA	9.75 ± 0.12 (8)	9.85 ± 0.12 (5)	9.73
Granite UFBA	1.80 ± 0.03 (10)	1.82 ± 0.01 (6)	1.76
Clay 1 IPT	1.53 ± 0.01 (9)	1.51 ± 0.01 (5)	1.56
Clay 2 IPT	1.95 ± 0.02 (6)	1.93 ± 0.03 (6)	1.94
Mn ore IPT 52	3.31 ± 0.03 (5)	3.41 ± 0.06 (5)	3.43
Bentonite CEPED	9.61 ± 0.27 (4)	9.50 ± 0.11 (5)	9.48
Mn ore CEPED	1.80 ± 0.01 (4)	1.83 ± 0.01 (5)	1.81

(*N*), determinations number.
*At 95% confidence level.

Table 6. Compositions of standards analysed

Standards	Fe_2O_3 (%)	Al_2O_3 (%)	SiO_2 (%)	TiO_2 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)
Andesite GSJ JA-1	6.95	14.98	64.06	0.87	5.68	1.61	3.86	0.82
Basalt GSJ JB-1a	9.10	14.51	52.16	1.30	9.23	7.75	2.74	1.46
Rhyolite GSJ JR-1	0.96	12.89	75.41	0.10	0.63	0.09	4.10	4.44
Rhyolite GSJ JR-2	0.86	12.82	75.65	0.09	0.45	0.05	4.03	4.48
Bauxite NIST 69 A	5.82	55.0	6.01	2.78	0.29	0.02	<0.01	<0.01
Basalt UFBA	9.73	14.9	56.3	1.10	7.42	4.37	2.53	2.15
Granite UFBA	1.76	14.60	71.6	0.26	1.24	0.46	3.75	4.91
Clay 1 IPT	1.56	45.0	30.7	1.40	0.07	0.13	0.06	1.26
Clay 2 IPT	1.94	38.4	45.1	0.24	0.07	0.14	0.01	0.85
Manganese ore IPT	3.43	10.6	3.06	0.28	0.15	0.25	0.10	1.60
Bentonite CEPED	9.48	20.7	—	1.18	0.48	2.47	0.51	1.18
Manganese ore CEPED	1.81	8.65	2.36	0.28	0.15	0.25	—	—

IPT, Instituto de Pesquisas Tecnológicas do Estado de São Paulo, Brasil.
GSJ, Geological Survey of Japan.
NIST, National Insitute of Standards and Technology, U.S.A.
CEPED, Centro de Pesquisa e Desenvolvimento de Bahia, Brasil.

The results are described in Table 5 and matrices compositions are shown in Table 6. Sample preparation of geological matrices[11] were made using hydrochloric acid, sulphuric acid and hydrofluoric acid. The reductor proposed was hydroxylammonium chloride, but ascorbic acid should be used. Hydroxylammonium chloride is better because its solutions are more stable than the ascorbic acid solutions, 50.0 mg of hydroxylammonium chloride are enough to reduce 25.0 μg of iron(III) to iron(II).

The *F* test[12] was applied to the results obtained with the procedures A and B, and it revealed that there is no significant difference in the precision of the two methods. The application of the paired *t* test[12] to the results obtained by the two procedures (Table 5) showed that there was no significant difference between the two methods at the 95% confidence level. The least-squares analysis, which is potentially the most useful statistical technique for the comparison of two proposed procedure,[13,14] was also used and it revealed that there was a good correlation ($r = 0.9998$) and that the calculated slope and intercept did not differ significantly from the 'ideal' values of 1 and 0, respectively, and thus there was no evidence for systematic differences between the procedures A and B described in the Experimental part. The analysis of variance[14] was applied to the results described in the Table 5. This test showed that there was no significant difference between TAN methods and certificate results.

The derivative procedure can be used for iron determination in freshwater.

CONCLUSIONS

Cations that interfere at ratios of 10–100 X that of Fe, such as Zn, Ti and Pb, which may occasionally be present at elevated levels in the same geological matrices, must be separated or if possible masked, otherwise the Fe results will be high. The proposed method can be applied to spectrophotometric determination of iron in matrices that do not contain significant amounts of interferents such as cobalt(II), nickel(II), copper(II) and mercury(II). Cobalt(II) is the main interferent in the iron determination with TAN. However, it is not a usual constituent of geological matrices.

The results of analysis in comparison with certified values of several matrices, indicating that the procedures provide accurate and precise results without the necessity of chemical separation. As a result, the proposed method is useful for routine analysis owing to its simplicity.

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