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Use of 9,10-Phenanthrenequinone Monoxime as a Selective and Sensitive Reagent for Iron in Environmental Samples

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9,10-Phenanthrenequinone monoxime (PQM) has been suggested as an analytical reagent for metals. The elements Fe(III), Ni(II), Cu(II) (KAMIL et al, 1978) and Co(II) (TRIKHA et al. 1967) have been determined in aqueous systems by liquid-liquid extraction in the microgram range through the use of PQM.

The usefulness of this versatile reagent has been extended to the analysis of trace amounts of iron in environmental, industrial efaluence, pharmacicular, and alloy samples by using a new technique of extraction, "solid-liquid separation after liquid-liquid extraction". The present communication deals with the analytical use of 9,10-Phenanthrenequinone monoxime. The reagent reacts with Fe(III) in the pH range 2.0-8.4 forming a brown coloured water-insoluble thermally stable complex. This coloured pigment is extractable into molten naphthalene. The solidified naphthalene containing iron complex was dissolved in chloroform. The absorption in the visible region varies linearly with Fe(III) concentration at 470 nm. This characteristic has been employed in the quantification of iron in a variety of samples.

MATERIALS AND METHODS

Doubly distilled water and analytical reagent grade acids and salts were used throughout unless stated otherwise. Ammonium ferric sulphate was prepared in water and standardized by usual method. A 0.001 M PQM solution was prepared in ethanol. Dilute solution of perchloric acid (0.1 M) and sodium perchlorate (1 M) were used for pH adjustments.

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Naphthalene and chloroform were checked spectrophotometrically before use.

An Elico meter, SP-700/500 spectrophotometer (Pye Unicam) and SP-191-atomic absorption spectrophometer (Pye Unicam) were used for measurements.

To an aliquot of iron(III) solution in a beaker, add 2.1 ml of the reagent solution. Measure the pH and adjust it to lie within the range 2.0-8.4 by adding 0.1 M perchloric acid solution or 1.0 M sodium perchlorate solution. Transfer the solution into a 100 ml round-bottom flask and heat to 60°C in a water-bath. Add 2.0 g of naphthalene, stopper the flask and continue to heat until the naphthalene melts. Remove the flask from the water bath and shake it vigorously until the naphthalene separates as a solid mass. Repeat the melting and solidification procedure. Separate the naphthalene from the aqueous phase by filtration through a filter paper. Dissolve the solid mass in chloroform and dilute to 10 ml with chloroform in a calibrated flask. Dry the solution with 2.0 g of anhydrous sodium sulphate to remove the last traces of water. Place a portion of this solution in 1 cm cell and measure the absorbance at 470 nm against a reagent blank. Prepare a calibration graph under similar conditions.

RESULTS AND DISCUSSION

The absorption spectra of PQM and its iron complex in naphthalene-chloroform solution were recorded against water and reagent blank respectively. It was observed that the complex absorbed strongly in the range of 468-474 nm where reagent absorbed negligibly.

Extractions were carried out over a wide range of pH. It was found that the extraction were quantitative over the pH range of 2.0-8.4.

The volume of the reagent was varied keeping to other conditions constant. It was observed that the absorbance remained constant for use of 0.5-5.0 ml of 0.001 M PQM solution.

Amount of naphthalene was varied from 0.2-4.0 g. It was found that the extractions were quantitative when the amounts of naphthalene were in the range of 1.3-3.5 g. Thus, 2.0 g of naphthalene was used in all the cases.

Since the volume of the organic phase is very small as compared with that of the aqueous phase, it was necessary to observe the effect of the volume of aqueous phase on the extractions. It was observed that the extractions were quantitative when the aqueous phase did not exceed 50 ml.

The absorbance of the extract after dissolution in chloroform was measured at a definite intervals of time. The absorbance remained constant for 25 h.

Extractions were carried out at different intervals of shaking time. It was found that the extraction was fast and took 2.0 min for complete extraction. Various electrolytes such as sodium chloride, sodium nitrate and sodium perchlorate in the concentration range of 0.01-0.1 M had no effect on extractions indicating no salting effect.

Under the optimum conditions described above, a calibration curve was constructed at 470 nm against a reagent blank. Beer's law was obeyed in the concentration range of 28.0-37.0 μg per 10 ml of the final solution. From the Ringbom plot it was found that 8.4-30.7 ppm of iron could be determined accurately. The molar absorptivity and sensitivity were calculated to be 2.067×10^3 $l.mol^{-1}.cm^{-1}$ and 0.027 $\mu g/cm^2$ respectively. Aliquots containing 11.2 μg of iron gave a mean absorbance of 0.405 with a standard deviation of 0.0032. The accuracy was checked by the analysis of iron in certain complex materials (Table 1).

In general, 5000 μg/ml of anions and 100 μg/ml of ions were added individually to aliquots containing 11.2 μg of iron. Among the anions (Table 2), orthophosphate, fluoride, citrate, tartrate and EDTA interfered, but their relatively lower amounts could be tetrated except EDTA probably due to higher stability of Fe-EDTA complex. Among the metal ions (Table 3) Co(II), Ni(II), Cu(II), Pd(II) and Os(VIII) interfered, but their relatively low concentrations could be tolerated by extraction of iron at pH = 2.0, while Pd(II) could be eliminated by extraction of iron at pH 8.4. Ru(III), Rh(III), Ir(III), Pt(IV) and Cr(III) form complexes with PQM after heating for about 30 min, while iron reacts immediately with PQM at room temperature, so they do not interfere in the determination of iron when each is present in 100 μg amount.

Table 1. Determination of Iron in Alloys, Beers, Wines, Environmental Samples, Human Hair and Ferrous gluconate.

Sample	Fe found by present method (μg/ml)	Average (μg/ml)	Error (%)	Fe found by AAS method (μg/ml)
Stainless steel No. 304	14.8,15.0, 14.8,14.8, 14.8	14.84	1.0	14.9
Stainless steel No. 306	20.0,19.8, 20.0,19.8, 19.6	19.84	0.8	20.0
33d Steel (MBS)	9.0, 8.9, 9.0,8.9, 9.0	8.96	0.44	9.0
Inconet 600	15.9,15.8, 15.6,15.8, 15.8	15.78	0.10	15.8
Elgiloy	15.0,15.1, 15.0	15.06	0.90	15.2
CPB-Lead concentrate	8.5, 8.4, 8.5,8.4, 8.5	8.46	0.47	8.5
CZM-1-Zinc concentrate	11.0,11.2, 11.1,11.0, 11.1	11.1	0.90	11.2
Beer A	4.1, 4.2, 4.2, 4.2 4.2	4.14	1.2	4.2
B	4.9, 4.9, 5.1, 5.0, 5.0	4.98	0.47	5.0
C	3.9, 3.8, 3.9, 3.8, 3.7	3.82	-0.50	3.8
D	6.5, 6.4, 6.5, 6.6, 6.4	6.48	0.30	6.5

Table 1(Cont.)

E	3.5, 3.6, 3.4, 3.5, 3.5	3.50	0.00	3.5
Wine A	6.1, 6.2, 6.2, 6.3, 6.1	6.18	0.32	6.2
B	5.9, 6.0, 6.0, 6.0, 6.0	5.98	0.33	6.0
C	5.1, 5.2, 5.3, 5.1, 5.2	5.18	0.38	5.2
D	5.4, 5.5, 5.4, 5.6, 5.5	5.48	0.36	5.5
E	4.5, 4.6, 4.6, 4.5, 4.7	4.58	0.43	4.6
Environmental Samples				
Flyash A	11.5,11.6 11.6,11.5, 11.6	11.56	0.34	11.6
B	11.9,11.8, 12.1,12.0, 12.0	11.96	0.33	12.0
C	10.5,10.4, 10.4,10.5, 10.5	10.46	0.38	10.5
D	13.0,12.8, 12.9,12.9, 13.0	12.92	0.61	13.0
Waster Water (Okhla seawage)				
A	4.8,4.7, 4.7,4.8, 4.8	4.76	0.83	4.8
B	4.5,4.5, 4.4,4.5 4.5	4.48	0.44	4.5

Table 1 (Contd.)

	C	4.9, 4.9, 5.1, 5.0, 5.0	4.98	0.40	5.0
Waste Water (I.P.thermal power)	A	4.9, 4.8, 4.9, 5.1, 5.2	4.98	0.40	5.0
	B	4.8, 4.9, 5.0, 5.0, 4.8	4.90	0.00	4.8
	C	5.9, 6.0, 6.1, 5.9, 6.0	5.98	0.33	6.0
	D	5.4, 5.5, 5.6, 5.4, 5.5	5.48	0.36	5.5
Human hair	A	13.8,13.9, 13.9,14.0, 14.0	13.92	0.57	14.0
	B	14.2,14.4, 14.4,14.6, 14.5	14.42	0.55	14.5
	C	14.9,15.0, 14.8,14.9, 15.0	14.92	0.52	15.0
	D	26.5,26.8 26.6,26.9, 27.0	26.76	0.88	27.0
Ferrous gluconate		12.0,11.9, 11.9,12.0, 12.0	11.96	0.33	12.0

Table 2. Effect of Diverse Anions
Fe : 11.2 μg/ml

Alkali salt added	Amount of anion added (μg/ml)	Absorbance at 470 nm
-	-	0.410
Sodium fluoride	5000	0.080
	1000	0.280
	500	0.390
	250	0.406
Sodium chloride	5000	0.408
Potassium bromide	5000	0.405
Potassium iodide	5000	0.405
Sodium carbonate	5000	0.410
Sodium thiocyanate	5000	0.404
Sodium sulphate	5000	0.412
Sodium orthophosphate	5000	0.389
	2000	0.405
Sodium oxalate	5000	0.406
Sodium citrate	5000	0.39
	2000	0.406
Sodium potassium tartrate	5000	0.385
	2000	0.408
EDTA (disodium)	5000	0.020
	1000	0.080
	100	0.080

Table 3. Effect of Diverse Metal Ions
Fe : 11.2 μg/ml

Metal salt added	Amount of metal ion added (μg/ml)	Absorbance at 470 nm
-	-	0.410
Cobalt(II) chloride	100	0.490*
	50	0.420*
	40	0.414*
Nickel(II) chloride	100	0.450*
	50	0.412*
Copper(II) chloride	100	0.46*
	50	0.430*
	30	0.410*

Table 3 (Contd.)

Palladium(II) nitrate	100	0.520+
	50	0.480+
	20	0.430+
	10	0.412+
Osmium(VIII) tetraoxide	100	0.450*
	50	0.430*
	30	0.412*
Ruthenium(III) chloride	100	0.412
Rhodium(III) chloride	100	0.413
Iridium(III) chloride	100	0.412
Platinum(IV) chloride	100	0.410
Chromium(III) chloride	100	0.412
Aluminium(III) nitrate	100	0.410
Lead(II) nitrate	100	0.405
Zinc(II) chloride	100	0.412
Cadmium(II) chloride	100	0.411
Mercury(II) nitrate	100	0.413
Silver(I) nitrate	100	0.412
Ammonium molybdate	100	0.412
Ammonium vanadate	100	0.410
Sodium tungstate	100	0.406
Manganese(II) sulphate	100	0.410
Ammonium arsenite	100	0.405
Tartar emetic	100	0.404
Gold(III) chloride	100	0.412

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*Eliminated by extraction of iron at pH 2.0.

+Eliminated by extraction of iron at pH 8.4.

Determination of Iron(III) in Alloys, Beers, Wines, Environmental samples, Human hair and Ferrous gluconate.

A 100 mg of the alloy sample was dissolved in 15-20 ml of aqua-regia and the solution evaporated to dryness. Then 10 ml of concentrated hydrochloric acid were added, the solution was warmed to dissolve salts and transferred to a 1 litre standard flask and made upto the mark with distilled water. An aliquot of this solution was taken in a beaker and extracted according to the general procedure.

A 50 ml of beer or wine sample was evaporated to dryness. The residue was ashed and dissolved in a 100 ml of 1:1 nitric acid solution. To avoid loss of iron by evaporation the ashing temperature was maintained at 560-580°C. Four ml of this sample solution were taken and analyzed by the present method.

A 10 g of fly ash sample of I.P. thermal power (New Delhi) was digested with nitric acid for half an hour and its solution was made in a 50 ml standard flask. Two ml of this solution were taken and analyzed according to the general procedure.

A 500 ml of the composite sample of waste water (Okhla seawage, I.P. thermal power, Shantivana, New Delhi) was reduced to 50 ml by evaporation in the presence of a few drops of nitric acid. Five ml of this solution were taken for the analysis of these samples.

Human hair (1.0 g) samples were ashed separately at 550°C in a furnance. The residues were dissolved in concentrated nitric acid (10 ml) and evaporated to dryness.

The residues thus obtained were treated with distilled water, transferred in a 25 ml standard flask by filtration and made upto the mark with distilled water. Five ml of each sample were taken and analyzed by the general procedure.

A 5.0 ml ferrous gluconate sample was heated with 20 ml of nitric acid to dryness and ashed at about 550°C. The residue was again treated with 15 ml of nitric acid, evaporated to dryness and finally treated with distilled water, transferred in 100 ml standard flask by filtration and made upto the make with distilled water. Three ml of this sample solution was taken and analyzed according to the general procedure.

In all cases the extractions were carried out at pH 2.0 where other metal ions did not interfere. Five replicate determinations of iron were made for each samples. The results obtained by the present method were compared with atomic absorption spectrophotometric method. The results obtained by both the methods are incorporated in Table 3.

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