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APPLICATION OF A REDUCING COLUMN FOR METAL SPECIATION BY FLOW INJECTION ANALYSIS
Spectrophotometric Determination of Iron(III) and Simultaneous Determination of Iron(II) and Total Iron

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SUMMARY

Iron(III) (3×10^{-6}—5×10^{-4} M) is determined in a flow-injection system by passage through a Jones reductor mini-column before spectrophotometric detection with 1,10-phenanthroline in citrate buffer, pH 5.0. The mid-range precision is $\leq 1.4\%$, at a sampling rate of 60 h^{-1}. Iron(II) and total iron are determined by splitting the injected sample so that a portion passes through the reductor column and a delay coil before both streams are recombined with the unreduced portion preceding the remainder of the sample to mix with the reagent for spectrophotometric detection. Two peaks are produced for each sample, the first being a measure of iron(II), the second of total iron.

The spectrophotometric determination of iron(II) is generally done with 1,10-phenanthroline as the chromogenic reagent [1]. This has also been the case for flow-injection methods based on spectrophotometric detection [2—5]. Total iron has been determined after reduction of iron(III) with ascorbic acid [2, 3], so that water and plant material can be analysed for total iron (0.1—30 mg l^{-1}). Iron(II) and iron(III) can also be determined separately. Bubnis et al. [3] used a similar procedure, with incorporation of a 2-way switching valve which allowed introduction of ascorbic acid to one of a pair of sample injections, thus giving peaks for iron(II) and total iron. This rather complicated system, requiring two sample injections, has been simplified by incorporating sequential spectrophotometric and atomic absorption spectrometric detectors into a simple flow-injection manifold [4, 5]; iron(II) is determined spectrophotometrically with 1,10-phenanthroline and the effluent from the optical cell is nebulized into an atomic absorption spectrometer for determination of total iron. Iron(II) and iron(III) have also been determined by f.i.a. with amperometric detection [6].

Iron(II) and iron(III) have recently been determined spectrophotometrically by synchronized sample injection into two parallel flow systems, in which iron(II) is determined with 1,10-phenanthroline and iron(III) with thiocyanate [7]. Two spectrophotometric detectors are used. There would be obvious advantages if the two flow streams could pass through a single

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detector, as described by Kagenow and Jensen [8], or if a single injection could be split into two channels for separate determinations [9, 10]. Most advantageous would be a combination of the two, in which a single injection is split into two channels, then returned to a single stream to pass in sequence through a single detector. The general idea of sequential determinations has been reviewed by Luque de Castro and Valcarcel [11]. The type of system described above has been applied to the simultaneous determination of species that produce a colour at different rates [12] (e.g., nickel and cobalt with 2-hydroxybenzaldehyde thiosemicarbazone). Masoom and Townshend [13] used a similar principle for the simultaneous enzymatic determination of sucrose and glucose.

It is possible to apply this principle to the simultaneous spectrophotometric determination of iron(II) and total iron (and therefore iron(III)) by f.i.a. The sample is split into two; one portion proceeds immediately to react with 1,10-phenanthroline while the other is diverted through a Jones reductor mini-column and a delay coil. It rejoins the original flow stream after the first portion has passed for spectrophotometric determination of both portions in the same detector. In this way, successive peaks for iron(II) and total iron are obtained.

The use of reductor mini-columns is particularly effective in f.i.a. Schothorst et al. have shown that unstable oxidation states of metal ions such as chromium(II) [14], vanadium(II) [14] and uranium(III) [15] are effectively produced, and that nitrate and nitrite can be reduced by chromium(II)-EDTA produced in such a column [16]. In this paper, reduction of iron(III) to iron(II) is achieved efficiently in a small Jones reductor column, with little effect on sample dispersion.

EXPERIMENTAL

Reagents

All chemicals were of analytical-reagent grade and deionized water was used throughout. A 1,10-phenanthroline solution (0.25% w/v) was prepared every 4 days by dissolving 0.625 g of 1,10-phenanthroline hydrochloride (BDH) in 250 ml of 0.05 M hydrochloric acid. Citrate buffers of different pH values were prepared by mixing appropriate volumes of 0.1 M citric acid and 0.1 M sodium citrate to give the desired pH values between 3.0 and 6.2 [17]. A stock solution containing 0.1 M each of iron(II) and iron(III) was prepared by dissolving 1.9881 g and 2.7030 g, respectively, of their chlorides in 100 ml of 0.1 M hydrochloric acid.

Apparatus

Preparation of the Jones reductor [18]. Zinc shot (BDH; 20—30 mesh) was sieved through a 22-mesh sieve, and 4 g of the retained zinc was stirred for 1 min with 1 M hydrochloric acid. The liquid was decanted, 30 ml of 0.25 M mercury(II) nitrate was added to the zinc, and the mixture was stirred

for 3 min. After being washed three times with water by decantation, the amalgam was added slowly to a 3.0-cm long glass tube (2.5 mm i.d.) until the required packing was achieved. An electronic vibrator was used to settle the particles uniformly. Water was passed through the column and the reductor was stored in this condition until required.

Flow manifold. The manifold used for the determination of iron(III) is shown in Fig. 1. A 4-channel peristaltic pump (Gilson Minipuls 2) was used, and iron(III) solutions were introduced via a Rheodyne RH-5020 injection valve (Anachem) with a sample loop of 40 μl. Two packed reactors (3 cm long, 2.5 mm i.d.) filled with glass beads (0.25 mm diameter) were inserted as shown in order to give a stable baseline [15]. Teflon tubing (0.5 mm i.d.) was used for the rest of the manifold. The absorbance was measured at 512 nm with a Cecil CE-373 spectrophotometer connected to a Tekman Labwriter TE 200 recorder.

Simultaneous determination of Fe(III) and Fe(II) was achieved by modifying the manifold shown in Fig. 1, by splitting the sample injected into two streams. The complete assembly is shown in Fig. 2.

RESULTS AND DISCUSSION

Determination of iron(III)

When deionized water was used as a carrier stream for iron(III) a precipitate formed in the reductor after a short time, almost certainly of the

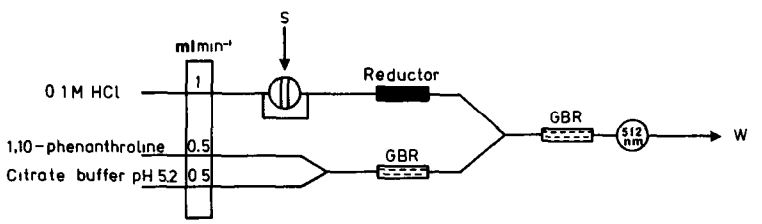


Fig. 1. Manifold used for the determination of iron(III): (S) sample injected; (GBR) glass beads reactor; (W) waste.

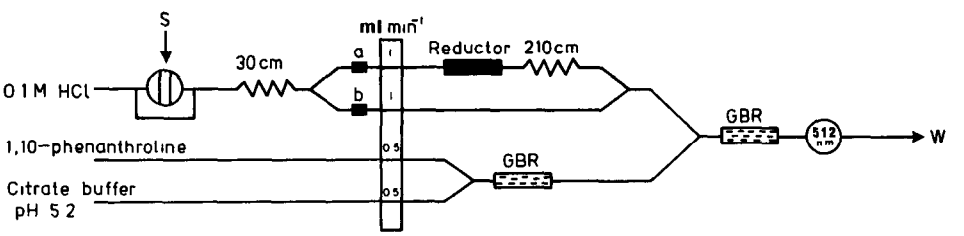
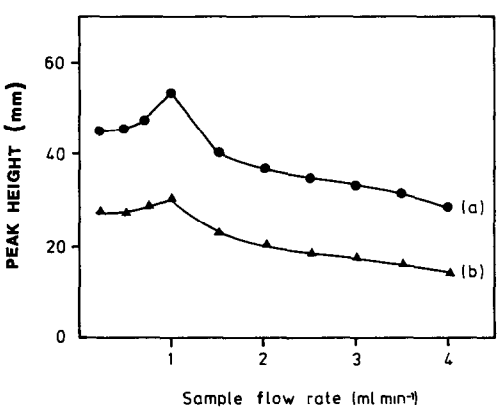


Fig. 2. Manifold used for the simultaneous spectrophotometric determination of iron(II) and total iron: (S) sample injected (40 μl); (a, b) pulse suppressors; (GBR) glass beads reactor; (W) waste.

hydrated oxide; 0.1 M hydrochloric acid was therefore used as carrier stream.

Four different buffer solutions were examined for use in the determination of iron(III) by reduction to iron(II). Acetate buffer was not satisfactory because it produced colours with iron(II) and iron(III). Phosphate and universal buffers were suitable, but small amounts of calcium interfered by precipitation when phosphate was used and the large number of constituents of universal buffer increases the opportunity for interfering effects. The most suitable buffer was citrate, which has the added advantage in that it can mask certain potential interferents [19, 20]. Citrate buffers were prepared in the pH range 3.0—6.2 [17]. The iron(III) responses were the same throughout this range. Therefore pH 5.2 was selected for further work. At this pH the effect of flow rate in the sample line on the determination of iron(III) was studied. The results are shown in Fig. 3. Initially, increasing the flow rate through the reductor column up to 1 ml min^{-1} was accompanied by increasing peak height. At higher flow rates, the absorbance decreased gradually, indicating that the reduction of iron(III) was then incomplete. Therefore 1 ml min^{-1} is recommended. It was necessary to include the two columns of glass beads into the system to give a more stable baseline.

Under the conditions established, the calibration results for iron(III) shown in Fig. 4 were obtained. The calibration graph was linear over the range 3×10^{-6}—5×10^{-4} M iron(III) with a regression coefficient for the 6 concentrations of 0.9996. The limit of detection (2× noise) for iron(III) was



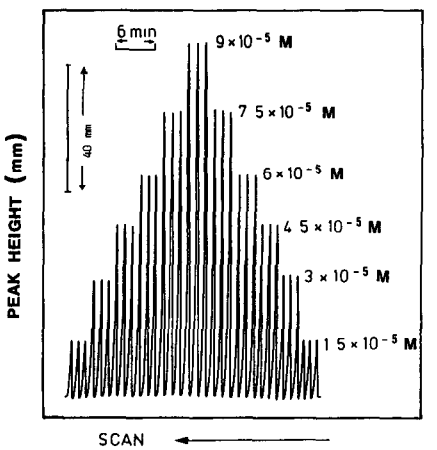


Fig. 3. Signal height for iron(III) as a function of flow rate through the reductor column: (a) 5×10^{-5} M, (b) 8×10^{-5} M iron(III). Manifold as in Fig. 1.

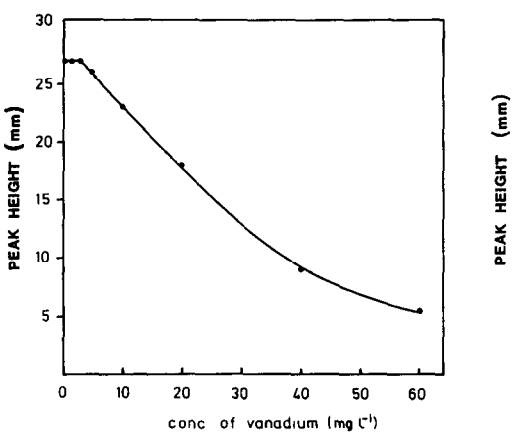
Fig. 4. Peaks obtained by injecting triplicate iron(III) standards of the concentrations stated. Manifold as in Fig. 1; sampling rate 60 h^{-1}.

3×10^{-6} M. The mid-range precision for 10 replicate injections was $\leqslant 1.4\%$. The sampling rate was 60 h^{-1}.

Interferences. Two groups of metals were studied for their interfering effects, first those elements in higher oxidation states which might be reduced in the Jones reductor, e.g., chromium(III), molybdenum(VI) and vanadium(V), and secondly, metals which have already been reported to interfere, e.g., copper(II), cobalt(II) and nickel(II) [2, 3]. Each metal ion was studied in the range 1—100 mg l^{-1} in a 1×10^{-4} M iron(III) solution in 0.1 M hydrochloric acid. No effects were apparent for cobalt(II), copper(II), nickel(II) and chromium(III) over the complete range of concentrations investigated. Citrate may be responsible for masking these metals. Vanadium caused decreased peaks when its concentration exceeded 2.5 mg l^{-1} (Fig. 5). When mixtures of iron(II) and vanadium were injected, the same depressions were obtained, indicating that the depression arises by competition between vanadium and iron(II) for the 1,10-phenanthroline, and not from involvement in the reductor column reactions. Molybdate interfered seriously. It formed a black precipitate on the reductor, and also gave a precipitate with the 1,10-phenanthroline.

Simultaneous determination of iron(II) and total iron

The simultaneous determination of iron(II) and total iron can be achieved by splitting the injected sample into two streams. The manifold is shown in



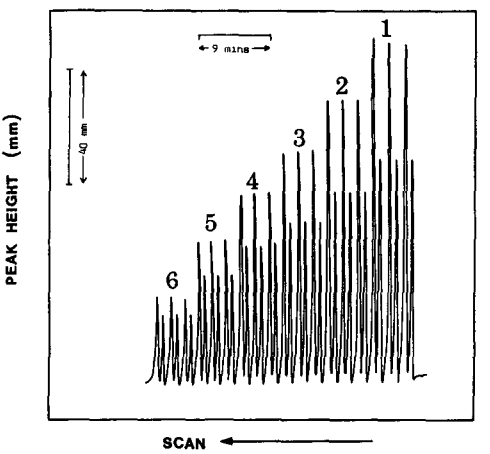


Fig. 5. Effects of vanadium on the peak height for 1×10^{-4} M iron(III).

Fig. 6. Typical calibration responses for simultaneous determination of iron(II) and iron(III) at the following respective concentrations: (1) 9×10^{-5} M, 5.5×10^{-5} M; (2) 8.5×10^{-5} M, 4.5×10^{-5} M; (3) 8×10^{-5} M, 3.5×10^{-5} M; (4) 7.5×10^{-5} M, 2.5×10^{-5} M; (5) 7×10^{-5} M, 1.5×10^{-5} M; (6) 6.5×10^{-5} M, 0.5×10^{-5} M. The second peaks in each pair represent total iron.

Fig. 2. One stream reacts directly with 1,10-phenanthroline, and then passes to the detector; this measures the iron(II) concentration. The other portion of the sample flows through the reductor column and a delay coil, and then rejoins the 1,10-phenanthroline stream to give a second peak completely resolved from the iron(II) peak. This peak is a measure of total iron, i.e. iron(II) and iron(III), in the original sample.

Reproducible splitting of the injected sample is not necessarily simple to achieve. Many means were investigated, which to a great extent were similar to those reported previously [9, 11—13]. In one case, the splitting device (a perspex Y-piece, angle between the two outflow lines 90°, i.d. 0.7 mm) was positioned after the point of injection, with the flow rate at 1 ml min^{-1}. The pump was placed before the injector. One portion of the sample passed through the reductor and was immediately mixed with 1,10-phenanthroline before passing to the detector. The other portion was delayed by a 400-cm coil before mixing with the reagent. This arrangement gave an irreproducible splitting ratio, varying between 5:1 and 3:1, and in some cases no splitting occurred. A 60-cm long coil was placed before the injection point to make the sample speed as constant as possible before splitting [10] and also the splitting was controlled by introducing a 3-key 3-way valve (Anachem) at the convergence point of the two streams before mixing with the reagent. However, these modifications were not successful nor was the use of the 3-way valve as a splitter.

The failure of these common splitting procedures is attributed mainly to the relatively slow flow of the sample stream which is required for complete reduction, compared to the flow rates (8.6 and 17.0 ml min^{-1}) used for splitting reported previously [9,10]. It might be possible to design a splitting manifold suitable for slow flow but it would require many long coils in many parts of the f.i.a. system, which would have very detrimental effects on the dispersion of the sample.

After extensive investigation, the arrangement shown in Fig. 2 was found to give the best results, in which the pump is placed after the splitter. The design of the splitter is not critical, and the splitting ratio is controlled by the use of pump tubes of various sizes. In this work, the splitting was achieved by means of the perspex Y-piece described above, and 1:1 splitting was obtained by using one pump tube of 0.8 mm i.d. connected to the reductor, and one of 0.5 mm i.d. for the other channel; this was checked by splitting standard solutions of iron(II). The 30-cm coil before the splitting point was still necessary to avoid the effect of variation of injection speed on sample splitting [10]. Pulse suppressors (0.02 in. i.d., Sterilin) were connected between the splitter and pump tubes to eliminate any effect of pulsing on the splitting ratio.

Typical calibration results for 40-μl injections of iron(II)/iron(III) standards are shown in Fig. 6. The first peak is a measure of iron(II), the second of total iron. The sample throughput was 40 h^{-1} with a relative standard deviation of 0.7—1.0% over the range shown in Fig. 6.

Conclusions

The incorporation of a reductor mini-column into the flow-injection system provides a simple means of determining iron(III) with 1,10-phenanthroline. Dispersion of the sample zone is little affected by the column. An improved method of sample splitting has been devised, which has allowed mixtures of iron(II) and iron(III) to be determined by using the same reagent and detector. This provides a much simpler method of analysis than those described previously, using f.i.a. or, probably, any other technique.

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