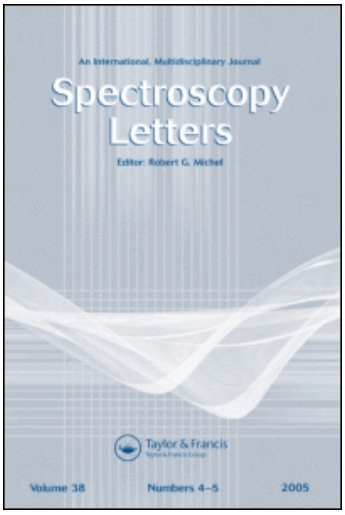

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Hydrodynamic Sequential Injection Spectrophotometric System for Determination of Manganese in Soil

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ABSTRACT A novel hydrodynamic sequential injection (HSI) spectrophotometric system for determination of manganese was developed. It is based on the complexation of Mn(II) with formaldoxime in basic solution ($pH \geq 10$) to produce product that could be monitored spectrophotometrically at 450 nm. Based on the HSI concept, both sample and reagents were aspirated through solenoid valves to fill a defined volumes conduit between 3-way connectors connected in series, forming stacked zones of solutions similar to those in normal SI. The concept was successfully demonstrated for manganese determination. A linear calibration graph over a range of 0.5 to 30 mg L^{-1} Mn(II) with a detection limit of 0.2 mg L^{-1} was obtained. Relative standard deviations for 11 replicated injections of 5 and 20 mg Mn L^{-1} were 5.6% and 2.4%, respectively. A sample throughput of 45 h^{-1} was achieved. The results from investigation of exchangeable manganese in soil samples by the developed method were found to be in good agreement with the results obtained by a batch spectrophotometric method, despite the proposed system employed simpler and more cost-effective devices/instruments, had higher degrees of automation with full microcontroller control of the operation, and consumed smaller amounts of chemicals (250 μL each of hydroxylamine, sample, and formaldoxime solutions and 2.5 mL of buffer carrier solution per operation cycle).

KEYWORDS formaldoxime, hydrodynamic sequential injection, manganese, soil, spectrophotometric

INTRODUCTION

Manganese is the one of essential micronutrients for plant growing. Manganese in soil may appear in different forms including dissolved, exchangeable, reducible, organic bound, and residual.[1] Dissolved and exchangeable manganese are an important form readily available for plant uptake.[2] Manganese deficiency in plants is shown by discoloration on lower leaves,[3] whereas the excess accumulation of manganese gives rise

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to the abnormal loss of leaves.[4] Consequently, various methods for soil analysis have been developed for quantitation of manganese.

Some official methods are based on spectrophotometric technique using periodate as a reagent and an atomic absorption spectrophotometric technique.[2] These techniques provide good accuracy and sensitivity, but consume large amounts of chemicals, take a long time, or require expensive instruments. Moreover, elevated temperature is required for the redox reaction of manganese and periodate to produce a colored product. For analysis of a large number of samples, flow-based methods that provide higher degrees of automation and better analytical features have been developed, such as flow injection (FI)[5–21] and sequential injection (SI).[22,23] FI technique, which operates in continuous flow mode, usually provides higher sample throughput, but with higher consumption of solutions. It is usually assembled requiring relatively simpler and lower cost devices. Multicommutation using a network of 3-way solenoid valves can make the FI system simpler and more versatile.[16,24] On the other hand, SI technique usually requires higher cost devices, such as high-quality syringe pump to meter precise volumes of solutions and a rotary selection valve for selection of different solutions, all under computer control. It is operated under programmable flow, thus minimizes volumes of sample, reagents, and waste. In this work, we introduce a new solution management procedure, the operation of which is similar to SI, therefore sample and reagents are sequentially aspirated to form stacked zones in a tubing while the carrier flow is halted. When the carrier flow starts to push the zones to a detector, zone penetration occurs in the same way as in SI, leading to mixing and the reaction to proceed. The introduction of solutions into tubing can be achieved by hydrodynamic flow concept[25] with use of cost-effective devices, solenoid valves and 3-way connectors, leading to the name hydrodynamic sequential injection analysis (HSIA).[26,27]

The two main detection techniques, visible spectrophotometric and atomic spectrophotometric, are usually employed in flow-based system for determination of manganese. For analysis of samples with low concentration of manganese ($\mu g\,L^{-1}$ to sub-mg L^{-1} levels) (e.g., freshwater and seawater), catalytic spectrophotometry employing oxidation reaction of periodate and various organic compounds with manganese acting as a catalyst[11–14,17] or atomic absorption/emission spectrophotometry with an on-line sorption column packing with 8-hydroxyquinoline,[21] iminodiacetate resin,[13] silica gel functionalized with 1,5-bis(di-2-pyridyl)methylene thiocarbohydrazide,[10] thiol resin,[9] or anion exchange resin[7] have been developed. Spectrophotometric detection based on oxidative conversion of Mn(II) to permanganate[5, 6, 16, 20, 22] or complex formation of Mn(II) with 4-(2-pyridylazo) resorcinol (PAR)[15] or formaldoxime[23] is widely used for manganese determination at mg L^{-1} level, such as in plant extract, wastewater effluent, and soil. The FI potentiometric method was also reported for determination of manganese in soil.[4]

In this work, we would like to propose a HSI spectrophotometric method for determination of manganese in soil. It is based on the reaction of Mn(II) and formaldoxime in basic solution to form the red-brown complex, which has a maximum absorption at 450 nm. By HSI concept, sample and reagents can be sequentially aspirated to place in a defined volumes conduit through solenoid valves and 3-way connectors under programmable control using a home-made controller unit. A linear calibration graph in range 0.5–30 mg Mn L^{-1} and detection limit of 0.2 mg Mn L^{-1} were obtained. Various advantages such as simple and cost-effective instruments used, rapid analysis with low chemical consumption, and high degrees of automation were gained.

MATERIALS AND METHODS

HSI Manifold

A schematic diagram of the proposed HSI system is illustrated in Fig. 1. The system consisted of a two-channel peristaltic pump (Alitea, Medina, WA, USA), 6 solenoid valves (Cole-Parmer, USA), a simple spectrophotometer (Spectronic 21, Bausch&Lomb, USA) equipped with a 10-mm pathlength flow-through cell (Hellma, Nuernberg, Germany) and a recorder (Linsies, NJ, USA). All tubing used PTFE tubing of inner diameter 0.5 mm, except Tygon pump tubing (Saint-Gobain Performance Plastics, NJ, USA). For automation by electronic control of the system, a home-made controller based on Basic Stamp II SX microprocessor (Parallax, USA) was employed for timing control of the operation of the solenoid valves.

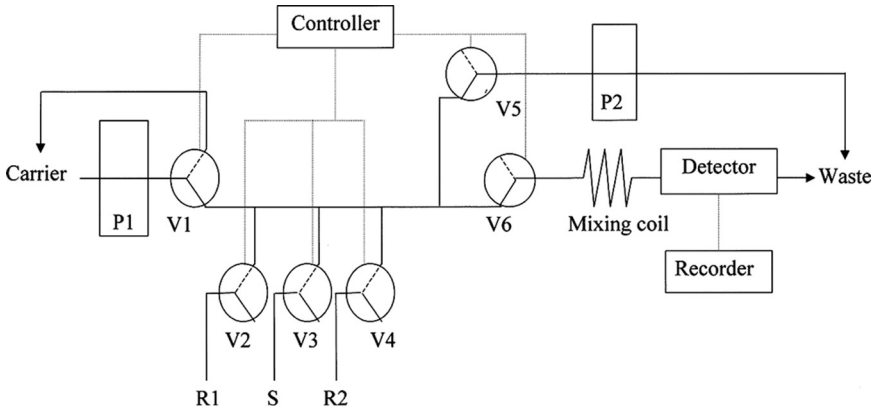

FIGURE 1 A schematic diagram of the HSI setup: V1 to V6 = solenoid valves 1 to 6; P1, P2 = peristaltic pump; R1 = hydroxylamine; R2 = formaldoxime; S = standard/sample; controller = a home-made controller unit.

Chemicals

Deionized water (Milli RX, Millipore, Bedford, MA, USA) was used throughout. All chemicals were of analytical reagent grade, unless otherwise stated. The chromogenic reagent, 0.6 mol L^{-1} formaldoxime, was prepared from the reaction of formaldehyde (M&B) (5.04 mL of 37% v/v) and hydroxylamine (Carlo Erba, Milano, Italy) (5.00 g) and adjusted the volume to 100 mL with water. A stock standard solution of 100 mg L^{-1} of Mn(II) was prepared by dissolving 0.0618 g of $MnSO_4 \cdot H_2O$ (Fluka, Buchs, Switzerland) in a portion of water. A 1.00 mL portion of concentrated nitric acid (Carlo Erba) was added before adjusting the volume to 200 mL of a volumetric flask with water. A 0.03 mol L^{-1} hydroxylamine solution was obtained by dissolving 0.21 g of the chemical in 100 mL of water.

The buffer carrier solution was prepared by dissolving 6.75 g of ammonium chloride (Carlo Erba) in 500 mL of water, and ammonia solution (BDH, Poole, Dorset, UK) was added until pH of the solution reached 10.2. Then, buffer solution was used to adjust the volume to 1000 mL with water.

Procedure

With the proposed manifold in Fig. 1, the operation sequence as shown in Table 1 was programmed to the controller. The operation sequence is briefly described as follows. First, the carrier solution was propelled by the peristaltic pump (pump channel 1) through solenoid valve 1, SV1, T-connectors, soleniod valve 5, SV5, and mixing coil to the flow cell of the detector. Then, by electronic control of the solenoid valves, the carrier stream was stopped (the carrier solution was redirected to its container) and hydroxylamine, standard/sample, and formaldoxime solutions were sequentially aspirated by pump channel 2 into the system to fill several defined volumes between the T-connectors to form stacked solution zones corresponding with the inlet port of each solution. An excess volume

TABLE 1 Operation Sequence of the HSI System (Fig. 1) for Determination of Manganese

Step	Valve	Interval(s)	Description
1	Turn off V1, V6		Stop the carrier flow
	Turn on V2, V5	5	Draw up hydroxylamine by P2
2	Turn off V2		
	Turn on V3	5	Draw up standard/sample (S) by P2
3	Turn off V3		
	Turn on V4	5	Draw up formaldoxime by P2
4	Turn off V4, V5		Stop aspiration of solution
	Turn on V1, V6	50	Carrier flow start to push the stacked zones to detector.
5	Turn off V1, V6		Return to step 1 to start next cycle

of each solution was discarded to waste. Finally, the carrier was allowed to push the stacked zones through the mixing coil to the detector while the signal profile was continuously recorded on the recorder.

Sample Preparation

Soil samples were collected at the depth of 15 cm throughout at least 3 points and mixed together. Soil extraction for exchangeable fraction of manganese was performed according to the reported procedure.[2] Briefly, a portion (10 g) of each sample was extracted with 100 mL NH_4OAc by shaking for 1 h. Then, it was filtered through a filter paper (Whatman no. 42). The filtrate was boiled to nearly dryness and continued until vapor of NH_4OAc ceased. Then, 2.00 mL HNO_3 and 1.00 mL H_2O_2 were added for digestion of organic matter, then, water added to a volume of 100 mL, the beaker was covered with watch glass and heated until dryness, 85% H_3PO_4 1.00 mL added, and the volume adjusted with deionized water to 100 mL.

RESULTS AND DISCUSSION

Effect of the Experimental Variables

In SIA, volumes of sample and reagents can be variably and accurately aspirated using a high-quality syringe pump and a selection valve. However, too large volume of the zones could reduce penetration of the sample and reagent zones leading to less reaction to occuring.[28] In HSIA, the volume of solutions was fixed by the defined volumes of the tube connected between the T-connector (about 50 µL each zone in this case), so a simple pump can be used for aspirating the solutions. Effect of the experimental variables such as carrier flow rate, mixing coil length, and concentration of reagents was studied.

Using preliminary condition (0.3 M formaldoxime, 0.06 M hydroxylamine, 100-cm mixing coil length, 0.1 M ammonia buffer pH 10 as a carrier), effect of carrier flow rate was investigated. Another peristaltic pump (P2 in Fig. 1) was employed for aspiration of the solution with constant flow rate (3 mL min^{-1}), while P1 was adjusted to give flow rate in the range 1–4 mL min^{-1}. A series of concentration of standard solution of manganese (0.5–20 mg L^{-1}) was injected and a calibration graph (a plot of peak height [mV] versus manganese concentration) was constructed in each case. Slopes of the calibration graphs of about 26 mV · L mg^{-1} were obtained for all flow rates. The flow rate of 3 mL min^{-1} was selected as it provided suitable sample throughput and was compatible with the aspiration flow rate.

The effect of mixing coil length (50, 100, 200, and 300 cm) was studied similar to that described above. Slopes of the calibration graphs obtained decreased significantly with the increase of the mixing coil length, due to higher dispersion of the product zone at longer coil. Thus, mixing coil length of 50 cm was selected as it provided higher slope and sample throughput.

Effect of chromogenic reagent, formaldoxime (concentrations 0.1, 0.3, 0.6, and 1.0 M) was investigated using the conditions previously selected. By considering slopes of the calibration graphs, it was found that formaldoxime concentration of higher than 0.3 M gives comparable sensitivities. Thus, 0.6 M formaldoxime was selected.

The reaction of Mn(II) with formaldoxime proceeds well in alkaline medium. Effect of pH of 0.1 M ammonia buffer (8, 9, 10, and 10.8) was investigated by injecting a series of concentration of manganese standard solutions (0.5–20 mg L^{-1}) with employing the above selected conditions. When pH changed from 9 to 10, a very sharp increase in sensitivity to reach maximum level (40 mV/mg L^{-1}) was observed. The pH of 10.2 was selected in order to ensure the sensitivity.

In basic solution, Mn(II) normally forms manganese hydroxide precipitate, which prevents it to react with formaldoxime. In order to avoid manganese hydroxide formation, hydroxylamine reducing agent was used. Effect of concentrations of hydroxylamine (0.01, 0.03, 0.06, and 0.10 M) was studied by carrying out the experiment similar to the above. Slopes of the calibration graphs increased with concentration of hydroxylamine and reached the plateau at 0.03 M hydroxylamine. Hydroxylamine (0.035 M) was then selected for further experiment.

It should be noted that the analog output of the Spectronic 21 spectrophotometer is linearly dependent with %T,(i.e., 1000 mV corresponded with 100 %T). Thus, a change of 40 mV should be equal to 4%T change or 0.018 absorbance units change. Therefore, the slope of a calibration graph of about 40 mV L mg^{-1} may be lower than in a batchwise

method, because in the continuous flow system the reaction may not reach equilibrium and sensitivity is controlled by extent of the reaction and degree of dispersion of the product.

Analytical Characteristics

Employing the selected conditions as studied in the previous section, a series of concentration of manganese standard solutions (0.5–30 mg L^{-1}) was injected into the HSI system. A linear calibration graph ($y = 37.6x - 13.1$, $r^2 = 0.999$) was obtained. A limit of detection (LOD)[29] of 0.2 mg L^{-1} and sample throughput of 45 h^{-1} were achieved. Relative standard deviations for 11 replicated injections of 5 and 20 mg Mn L^{-1} were 5.6% and 2.4%, respectively. The procedure consumed 250 μL each of hydroxylamine, sample, and formaldoxime solutions and 2.5 mL of buffer carrier solution per operation cycle. Analytical features of the developed method in comparison with the previously reported methods are summarized in Table 2.

Recovery of the method in the determination of exchangeable manganese in soil was evaluated by spiking manganese standard solution into the extracted solutions. Concentrations of manganese in the extracts were found in range 0.9–3.2 mg L^{-1}. Percentage recoveries in the range 91–110 were observed.

TABLE 2 Analytical Features of the Developed Method in Comparison with the Previously Reported Methods

Technique	Sample	Principle	Linear range (mg L^{-1})	LOD (mg L^{-1})	%RSD	Injection per hour	Ref.
SI-poten	Soil	Redox reaction of Mn(II) and hexacyanoferrate(III) leading to potential change of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ potential buffer solution	0.01–5.5	0.01	1.9 (0.33 mg L^{-1})	20	[4]
FI-spect	Mineral premixes and feedstuffs	Oxidation of Mn(II) to permanganate by periodate in slightly alkaline medium and in the presence of pyrophosphate and acetate	0–30	0.08	0.6 (10 mg L^{-1})	120	[6]
SI-spect	River water and effluent streams	Speciation of Mn(II) and Mn(VII) using 4-(2-pyridylazo) resorcinol, detected at 500 nm	0.02–0.50	0.005	0.3	30	[15]
Monosegmented flow spect	Soybean digests	Oxidation of Mn(II) by periodate in phosphoric acid medium to form permanganate anion	2.5–40.0	1.2	0.3 (17 mg L^{-1})	50	[16]
FI-spect	Natural water and effluent streams	Mn(II) was oxidized to permanganate by solid lead (IV) dioxide suspended on silica gel beads, detected at 526 nm	1.0–5.0	0.6	1.8	—	[20]
SI-spect	Tap water and effluent streams	Mn(II) was oxidized to permanganate by solid lead (IV) dioxide suspended on silica gel beads	1.0–7.0	0.6	3	50	[22]
SI-spect	Water	Formation of Mn(II)–formaldoxime complex using merging zone technique	0.5–4.0	—	6	36	[23]
HSI spect	Soil	Formation of Mn(II)–formaldoxime complex	0.5–30	0.2	2.4 (20 mg L^{-1})	45	This work

poten, potentiometry; spect, spectrophotometry.

Determination of Exchangeable Manganese in Soil Samples

Soil samples from longan orchards were analyzed for exchangeable manganese contents by the proposed method. Soil-extracted solutions were prepared as described in the "Sample Preparation" section. The solution was injected into the system, and concentration of manganese in the solution was calculated from peak height obtained using a calibration graph. Exchangeable manganese contents in soil ($\mu g\,g^{-1}$) were then calculated as summarized in Table 3. Analysis of the soil solution by the standard spectrophotometric method based on periodate reaction[2] was also carried out for comparison. Manganese contents found by using hydrodynamic injection method (x) agreed well with those found by the standard spectrophotometric method (y), indicated by the slope, intercept, and correlation coefficient (r) of the correlation graph between the two methods are close to 1, 0, and 1, respectively ($y = 1.2x - 3.0$, $r = 0.992$). According to the paired t-test at 95% confidence level,[29] there is no significant difference of the results from the two methods.

TABLE 3 Amounts of Exchangeable Manganese in Soil Samples

	Amount of exchangeable Mn in soil ($\mu g\,g^{-1}$)	
Sample number	Proposed method	Standard method[2]
1	10.7±1.0	9.5
2	8.7±1.0	8.5
3	7.7±0.8	8.5
4	16.7±2.1	12.2
5	11.7±1.0	8.5
6	13.7±2.1	8.5
7	8.7±0.8	6.9
8	68.3±1.3	79.0
9	98.1±1.3	116.8
10	30.6±2.5	36.2
11	42.0±2.1	51.2
12	26.6±1.3	30.9
13	34.5±2.5	41.6
14	17.7±1.3	19.1
15	13.7±1.3	12.2
16	11.2±1.0	14.9
17	8.7±0.8	9.5
18	8.7±0.8	8.5

CONCLUSIONS

A spectrophotometric method with a new HSI approach is introduced. The method is investigated for the determination of manganese based on the complex formation reaction of Mn(II) with formaldoxime giving a product that could be monitored for absorbance at 450 nm. The HSI provided introduction of precise and accurate volumes of sample and reagents to the flow system, even with use of a simple peristaltic pump, solenoid valves, and a simple controller. Various advantages similar to a typical SI system, such as low consumption of reagent solutions, low waste emission, and high automation, were gained. Application of the developed system to determination of exchangeable fraction of manganese in soil is demonstrated.

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