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Improved method for the determination of manganese in nuclear power plant waters

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ABSTRACT

An improved method for manganese determination in nuclear power plant waters has been developed. This method combines a selective chelation concentration method with a unique analytical separation for manganese from the interfering matrix using a weak acid cation exchange column. The detection sensitivity by conventional post-column derivatization is improved with the combination of chemical eluent suppression and subsequent post-column derivatization. The detection limit for manganese in ammonium matrix is approximately 2 pg/ml and the limit of quantitation 10 pg/ml with 100 ml sample volume.

INTRODUCTION

During the past decade, ion chromatography (IC) has been the primary analytical method for monitoring trace ionic impurities in power plant waters such as chloride, sulfate, organic acids and recently, manganese [1,2]. It has been reported that on-line monitoring of soluble manganese could be used effectively as an indicator of feed water corrosion product transport in nuclear power plants [2]. This report has brought attention to the existing corrosion monitoring techniques which are semiquantitative and time consuming. The Electric Power Research Institute, ERI, has recommended the monitoring of iron in power plant waters [3]; however, only 40% of total iron (pH > 7) is soluble. On the other hand, more than 90% of manganese is soluble and real-time corrosion monitoring is possible. As the new concept has received significant attention, an improved method for on-line manganese monitoring is being explored. Due to the fact that manganese concentration can be as low as 40 pg/ml in feedwater containing ammonia or morpholine, an improved method for manganese monitoring is required. It has been suggested that the required manganese detection limit and limit of quantitation must be 5 pg/ml and 50 pg/ml, respectively. The current IC suppressed conductivity method [2] for manganese shows detection limits of 50 pg/ml.

This paper will describe the development of a method for the determination of manganese in power plant waters. Sample concentration makes use of a chelating resin to more selectively concentrate manganese. Separation is accomplished on a carboxylate ion-exchange stationary phase which allows elution of manganese and other alkali metal and alkaline earth cations with a simple acid eluent. The detection mode involves a post column derivatization followed by visible detection to obtain pg/ml Mn detection limits. The use of a cation suppressor after the separator column and before the post-column system allowed the use of a weak com-

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plexing agent to improve manganese separation from other interfering transition metals.

BACKGROUND

The existing analytical chromatographic methods for manganese combine cation-exchange separation with suppressed conductivity, or mixed-bed ion-exchange chromatography with post-column derivatization [1]. The sample concentration mode commonly used is cation-exchange concentration. Most of the cation concentrator columns are made of low capacity, sulfonic acid, ion-exchange materials which are not particularly selective for manganese over other common cations. Concentration methods with this type of resin have been limited to a maximum of only 50 ml of sample due to high concentrations of ammonium and/or morpholinium relative to the manganese concentration. The limitation on concentration volume directly affects method detection limits. In addition, the elution of concentrated divalent cations from the cation concentrator to the analytical system requires divalent eluent components such as diaminopropionic acid (DAP) or ethylenediamine, or chelating eluent components such as oxalic acid, tartaric acid or pyridine 2,6-dicarboxylic acid [4]. These complexing agents degrade detection limits for manganese by suppressed conductivity or post-column derivatization.

In order to improve upon the manganese detection limit obtained by the existing IC method, the following factors must be considered. A selective concentration method for manganese is required in order to concentrate manganese from a large amount of sample containing interferences such as ammonium and morpholinium ions. The kinetics of divalent cation-exchange reaction should be relatively fast and column capacity should be relatively high so that a high sample flow-rate can be used to minimize sample loading time. It is very important that the concentration chemistry does not require resin regeneration or a chemical matrix elimination step, which normally leads to a high analytical blank. Also, the choice of the analytical column is very important. The elution chemistry of the concentrator column must be compatible with the analytical column such that the eluent used for removing the concentrated manganese from the concentrator is also useful for analytical separation. Finally, the detection method must be sensitive so that a relatively small sample preconcentration volume is needed to meet the detection limit requirements.

Sample concentration method

The choice for the ion-exchange concentration method usually depends upon the sample matrix complexity, ion-exchange selectivity and ion-exchange capacity. Generally, a low-capacity, non-selective cation-exchange concentrator column (*e.g.* sulfonate type) is commonly used for analyte concentration from relatively clean matrices [1,2]. As the sample matrices become more complex, a selective concentration method is required [5].

Although a sulfonate-type cation-exchange concentrator column has been used successfully to concentrate manganese [2], the combination of the ammoniated or morpholinated matrix of the power plant water combined with the detection limit requirements suggest that the sulfonated concentrator wil not be satisfactory. The ammonium or morpholinium in the matrix acts as an eluent during concentration causing breakthrough of the manganese and limits the maximum volume of sample that can be concentrated. Since the imminodiacetate concentrator is highly selective for manganese as compared with ammonium and morpholinium, there should be no matrix limitation on the concentration volume.

Analytical separation system

Three types of ion-exchange stationary phases are available for cation separations, strong acid cation-exchange sulfonate type, weak acid cation exchange carboxylate type and mixed cation and anion exchange. Strong acid cation exchange requires either a divalent component in the eluent which limits the maximum concentration volume on the concentrator column, or requires a chelating component in the eluent which compromises the detection system. Mixed-bed ion-exchange systems are used with an eluent containing chelating components to improve the separation of divalent cations. In this way divalent cations are separated both as free cations and as anionic complexes. This system gives the most control over selectivity for multicomponent cation separations but compromises detection sensitivity due to a competition between the eluent–cation complex and the detection reagent–

cation complex. The most promising ion-exchange stationary phase for cation separation allowing the detection limits required for manganese is the weak acid carboxylate ion exchanger. It is possible to separate and elute monovalent and divalent cations from this type of resin with just a simple acid eluent due to its high selectivity for hydronium ion. Although it does not afford the selectivity control of mixed-bed ion-exchange systems it does offer the potential for the necessary separation selectivity for manganese from other transition metals and the simple acid eluent should not interfere with the post-column detection system.

Detection method

Suppressed conductivity detection is currently used for divalent detection including manganese [1,2]. This detection method provides only low to moderate sensitivity for manganese, thus, a large sample preconcentration is required. A benefit, however, is that some of the co-eluting metals, such as Zn and Ni, are hydrolyzed and removed by the suppressor due to the high pH environment of the suppression reaction and these elements do not interfere with manganese detection.

Currently, at least 60–80 ml of sample are concentrated to obtain quantitation limits of 150 pg/ml (9–12 ng total) Mn by suppressed conductivity. With this detection system, lowering the limits of quantitation from 150 pg/ml to 10 pg/ml Mn would require at least 900 ml of sample to be concentrated. The analysis time using this method would be at least 2 h per sample.

A post-column derivatization method can be used to lower the detection limits of manganese. Many colorimetric reagents used for manganese determination are very selective and sensitive; however, the reaction rates are too slow for a dynamic post-column derivatization system. Most of these reagents form neutral, water-insoluble complexes with manganese. The well known water-soluble fluorimetric reagent for manganese determination, 8-hydroxyquinoline-5-sulfonic acid, does not give the required sensitivity for Mn because the kinetics are too slow. Formaldoxime has been reported as a useful colorimetric reagent for manganese determination using flow injection analysis [6]; however the sensitivity reported by this method is only 100 ng/ml for Mn. Another candidate is pyridylazoresorcinol (PAR) which has been commonly used for trace transition metal detection [7]. This method provides an excellent selective and sensitive detection method for Mn in high ammonium or morpholine matrix. Our preliminary experiments showed that only 500 pg of Mn are required to obtain the same detection sensitivity as 9000 pg by suppressed conductivity detection. Therefore, the sample volume required to obtain identical levels of quantification can be reduced by at least 18 times. The maximum absorption ratio of the Mn–PAR complex is found at 530 nm.

EXPERIMENTAL

All chromatography was performed on a Dionex (Sunnyvale, CA, USA) DX-300 chromatographic system equipped with two quaternary gradient pumps (AGP), a reagent-delivery module (RDM), a conductivity detector module (CDM-II), a variable-wavelength detector module (VDM-II) and a basic chromatography module. One of the gradient pumps was used to deliver eluents to the system. The other gradient pump was used as a sample pump. The on-line ion chromatograph series 8100 was used at Virginia Electric and Power Company (Surry, VA, USA). The Dionex columns used include the MetPac CC-1 concentrators (25 mm × 3 mm, 35 mm × 4 mm and 50 mm × 4 mm) and IonPac CS 12. For simultaneous detection of alkali, alkaline earth and Mn, the post-column system was replaced by Cation Micromembrane Suppressor (CMMS-II) and CDM-II. The eluent suppression with subsequent post-column derivatization detection used to improve Mn detection was accomplished by placing the CMMS-II between analytical column and post-column system. Data was collected and processed using Dionex AI-300 (8100 on-line system) or AI-450 software (DX-300 system).

The separation was accomplished on a Dionex IonPac CS12 column. Chromatographic conditions are listed in Table I. The HCl and pyrophosphoric acid eluents were prepared with ultrapure grade concentrated HCl (SeaStar Chemicals, B.C., Canada) and 97% pyrophosphoric acid (Aldrich, WI, USA). The standard solutions were prepared by dilution from stock 1000-mg/l atomic absorption grade with 18 MΩ cm deionized water.

TABLE I

CHROMATOGRAPHIC CONDITIONS

Concentrator	MetPac CC-1
Sample flow	5–10 ml/min
Eluent	10 m*M* HCl—8 m*M* pyrophosphoric acid
Eluent Flow	1.0 ml/min
Detection	
(1) Suppressed conductivity	
Eluent suppressor	Cation MicroMembrane Suppressor (CMMS)
Regenerant	100 m*M* Tetrabutylammonium hydroxide
Regenerant flow	5–10 ml/min
Detector	CDM-II
(2) Post-column derivatization	
Post-column reagent	0.4 m*M* Pyridylazoresorcinol 1.0 *M* Dimethylethanolamine 0.3 *M* Sodium hydrogencarbonate
Post-column device	Membrane reactor
Post-column flow	0.5 ml/min
Detector	VDM-II, 530 nm

RESULTS AND DISCUSSION

Chelation concentration

Iminodiacetate (IDA) chelating resin is known for its high selectivity for transition and post transition metals *vs.* alkali and alkaline earth metal cations [8,9]. At pH between 4.0 and 6.0, most of the transition metals are strongly retained by the resin, while the alkali and alkaline earth metals are only partially retained. The rate of exchange of metal cations and IDA is not diffusion-controlled, but governed by the rate of the chelation reaction itself [10]. Many reports have concluded that most divalent metal ions exhibit maximum distribution coefficients at pH 4.5 [11]. The selectivity coefficients for this resin relative to calcium are 4.9 for Mn, 20.5 for Co, 19.8 for Zn, 52 for Ni and 500 for Cu [12]. It has also been demonstrated that the resin acts as a tridentate ligand, forming a very stable metal complex which coordinates through the imino nitrogen atom and bonds through the two carboxylic oxygen atoms. This chelate formation involves the deprotonation process of carboxylic oxygen atoms [13–16].

The IDA resin has been used for several applications, particularly the separation/matrix elimination of transition metals from alkali and alkaline earth metals as a function of pH [5,8,9]. Only a few reports indicate metal uptake by the IDA in acid form since the conventional IDA-resins, Dowex A-1 (Dow Chemicals), and Chelex-100 (Bio-Rad Labs.) shrink considerably at low pH, and the exchange rates are subsequently limited by diffusion processes rather than chelation reaction [17].

A unique IDA resin prepared by incorporating IDA on 20-μm macroporous polystyrene–divinylbenzene substrate showed a behavior similar to that of the conventional chelating resins. The exchange rate of this material is controlled by the chelation reaction, and because of its structural rigidity, it is not limited by diffusion processes at low pH. This fully functionalized, high-capacity resin was used to pack the MetPac CC-1 metal concentrator column. The MetPac CC-1 was used to concentrate samples at up to 10.0 ml/min. The selective concentration of manganese from high concentrations of alkali–alkaline earth metals, ammonium, and morpholine was accomplished by acidifying the sample with 0.1 to 1.0 m*M* of an ultrapure acid. It was found that the presence of a low concentration of hydronium ion reduced the distribution coefficients of the matrix components; however, it did not significantly affect the manganese retention. The concentrated manganese was efficiently removed from the column in a tight band with as little as 20 m*M* HCl, enabling the column to be easily coupled directly to a low capacity cation separator column.

In an effort to maintain the maximum sensitivity, the effect of the concentration step on chromatographic efficiency for manganese was determined by comparing peak widths and heights obtained from the separation following preconcentration with those following direct injection. In the concentration mode, 100 ml of 20 pg/ml Mn (2.0 ng total) in 0.5 m*M* acetic acid were concentrated at a flow-rate of 9.9 ml/min, eluted from the MetPac CC-1 to the IonPac CS12 and then to the post column system. In the direct injection mode, 50 μl of 4.0 μg/ml Mn standard (2.0 ng total) were injected directly into the system and the peak width and heights were compared with that of the concentration mode. It was found that peak widths and heights were comparable in both modes.

The column capacity and dynamic range of sample concentration were evaluated by concentrating various amounts of sample containing fixed amount of manganese. Overloading the column capacity with a large amount of sample would result in nonlinear response. In this experiment, various volumes of sample containing 10 pg/ml Mn in 6.0 μg/ml ammonium (ammonium hydroxide) were employed. This sample represents a 1:60 000 mass ratio of Mn to ammonium ion. The sample was acidified with 1.0 *M* ultrapure acetic acid to make 0.1 m*M* concentration of acetic acid in the sample. Sample volumes ranging from 50 to 400 ml were concentrated on 25 mm × 3 mm and 35 mm × 4 mm MetPac CC-1 columns. Good linearity was observed. In addition, the *x*-intercepts in both cases are almost equivalent. Both sets of data indicate the minimum preconcentration volumes required by the two column dimensions are 7.9 ml for 25 mm × 3 mm and 9.0 ml for 35 mm × 4 mm. The slightly higher sample volume required by the 4 mm × 35 mm column is probably due to the higher dead volume producing band dispersion in the column. Also, this set of data may be used to estimate the detection limits of the two systems at 79 pg and 90 pg for 25 mm × 3 mm and 4 mm × 35 mm, respectively. The higher-capacity MetPac CC-1, 50 mm × 4 mm column, also gave excellent linearity and was used extensively in power plant as discussed later in this text.

Analytical separation

The IonPac CS12 column was used to separate manganese from ammonium and interfering transition metals that may present in the power plant samples. The CS12 is composed of an ethylvinylbenzene–divinylbenzene substrate polymer of very high cross-linking, onto which is grafted a weak acid carboxylate ion-exchange polymer active layer [18]. The highly cross-linked substrate core provides good mechanical stability for changes in ion-exchange form and compatibility with common HPLC eluent solvents.

Using HCl as an eluent on the CS12, manganese was only partially separated from Zn and Ni. Although Zn and Ni are present in very low level in these samples, the peak integration for manganese becomes difficult. The eluted Zn can be eliminated before the post-column system by inserting a CMMS between the IonPac CS12 and the post-column system. The CMMS hydrolyzes zinc and the hydrolysis products are either removed in the suppressor or do not react with the post column reagent.

The selectivity of the IonPac CS12 column can be altered by using a weak complexing agent such as pyrophosphoric acid (PPA). The combination of HCl and PPA eluent cleanly separate Mn from Zn and Ni. Although the PPA is not available in ultrapure grade, it was found that manganese contamination in this reagent is very low. The combination of HCl and PPA eluent with post-column derivatization has been used extensively at Virginia Electric and Power. Typical system blank and detection of 10 pg/ml Mn are shown in Fig. 1.

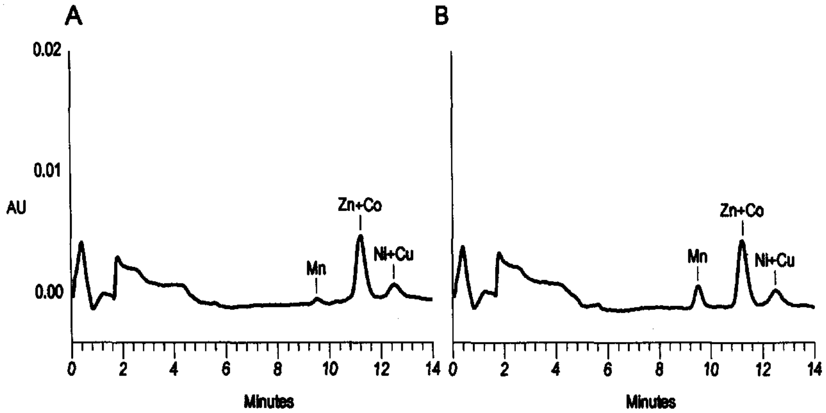

Fig. 1. Separation of Mn and other transition metals. (A) System blank, (B) 100 ml of 10 pg/ml Mn. Eluent: 10 m*M* HCl–8 m*M* PPA. Chromatographic conditions are listed in Table I.

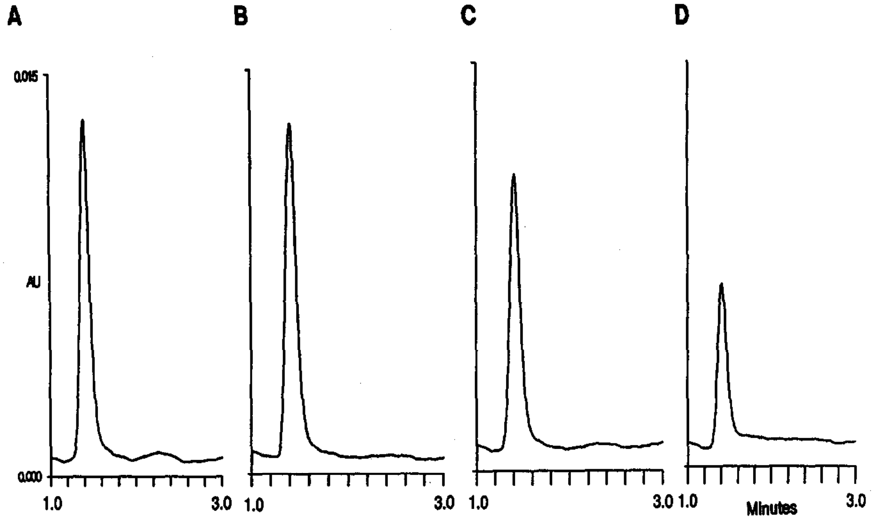

Fig. 2. Detectability of Mn in various eluents by PAR post-column derivitization. (A) 20 m*M* HCl, (B) 40 m*M* HCl–10 m*M* diaminopropionic acid, (C) 10 m*M* HCl–8 m*M* PPA and (D) 6 m*M* pyridine-2,6-dicarboxylic acid.

Detection method

Using complexing eluent modifiers such as pyrophosphoric acid, oxalic acid or pyridine-2,6-dicarboxylic acid normally result in loss in sensitivity by post-column detection as discussed earlier. The results from flow injection analysis for Mn, using PAR reagent, to determine the loss of sensitivity using different eluents is shown in Fig. 2. The experiment was performed by preparing 100 ng/ml Mn in various complexing eluents. A 50-μl volume of these solutions was injected into the eluent stream followed by post-column and visible detection at 530 nm. The order, from left to right, follows the increase in formation constant of Mn with complexing eluent (*i.e.* HCl < acid < pyrophosphoric acid < pyridine-2,6-dicarboxylic acid) indicated by the trend of decreasing sensitivity. An additional experiment was performed to confirm the competition reaction between the eluent and PAR by placing a CMMS-II between the separator column and the post column system. The eluent used was 10 m*M* HCl–8 m*M* PPA. The CMMS-II served as an eluent suppressor, removing the pyrophosphate anion and replacing it with hydroxide, forming water. Once pyrophosphate was removed, the sensitivity loss due to a competition reaction with PAR did not occur and essentially most of the manganese reacted with PAR. Fig. 3 shows the 50-μl direct injection of Mn and comparison of Mn detection response with and without eluent suppression before post-column derivatization. The elution order is slightly changed as compared with that of Fig. 1 because the MetPac CC-1 was not used. Interestingly, many metals were hydrolyzed in the basic environment of the suppressor and the hydrolysis prod-

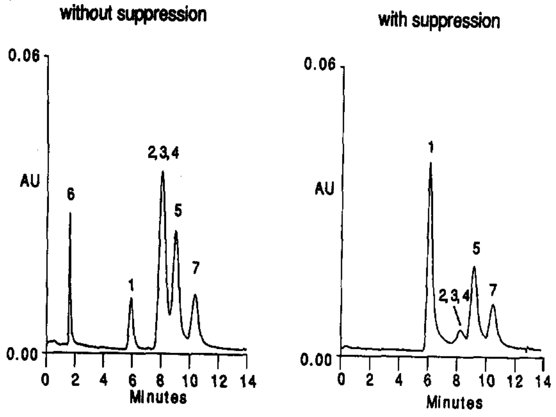

Fig. 3. Improved PAR post-column detection by eluent suppression. (A) Without eluent suppression and (B) with eluent suppression. Peaks: 1 = Mn (2.0 μg/ml); 2 = Cu (0.5 μg/ml); 3 = Cd (0.5 μg/ml); 4 = Zn (2.0 μg/ml); 5 = Co (2.0 μg/ml); 6 = Fe(III) (10 μg/ml); 7 = Ni (2.0 μg/ml).

ucts were removed by the suppressor or not detected by the post-column detection. This observation may be useful for using the suppressor as a sample preparation device.

The new improved method for Mn was installed at Virginia Electric and Power (Surry, VA, USA) and has been currently used for Mn monitoring. The chromatographic conditions was identical to that shown in Table I. The detection method used was eluent suppression with subsequent post-column derivatization. Typical detection limits obtained by this system is approximately 3 pg/ml (240 pg total) for 80 ml sample concentration.

Analytical precision and detection limits

The precision of the analysis was determined to establish the detection limits and limits of quantitation of this method. Deionized water (18.2 MΩ cm) was first purified to remove trace manganese, if present, by passing it through the MetPac CC-1 (50 mm × 4 mm, two columns in series), and the column effluent was collected in acid-cleaned PTFE bottles. The purified water was then analyzed for a manganese blank before it was used for standard preparation. Next, the standard 6 μg/ml ammonium was prepared from ultrapure ammonium hydroxide solution by dilution with the purified water and the solution was analyzed for manganese contamination. Finally, the 100-ml sample containing spiked with 10 pg/ml manganese in 6 μg/ml ammonium (1:60 000 mass ratio) was concentrated on the 35 mm × 4 mm MetPac CC-1, and separated using the chromatographic conditions listed in Table I. Statistical evaluation of three times standard deviation was used to obtain the detection limits of 1.2 pg/ml (120 pg total) for Mn. These data agrees well with the estimated detection limits by dynamic range study indicating 90 pg.

Application

Manganese mass transport. In a mass transport study conducted at Surry Power Station, the goal was to employ the new manganese method to monitor key sample points to identify corrosion rates. Fig. 4 shows the Mn mass transport of the feedwater (FW), main steam (MS), high-pressure heater drain (HPHD), condensate (COND) and polisher effluent (PE). The detail discussion of these components and mass transport rate can be found in the previous report [2].

The FW consists of 64% PE and 28% HPHD, with the remaining 8% from various drips from the MS. The total FW flow is 4.9 · 10^6 kg/h. The HPHD originates from MS that is used to reheat steam directed to the high-pressure turbine. The "spent" steam condenses to a collection tank then being pumped forwarded in the FW train. The HPHD flow is 1.4 · 10^6 kg/h which is 28% of the generated MS. The remaining portion of MS is the motive force used to turn the turbines to generate the pro-

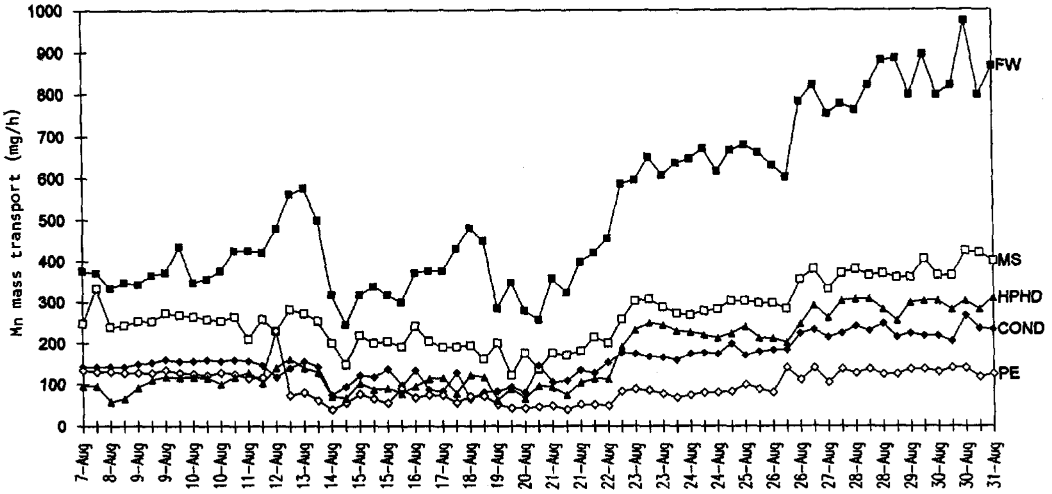

Fig. 4. Manganese mass transport data (mg/h). See text for abbreviations.

duced electricity. The "spent" steam then condenses back to liquid form (COND), and then "polished" as it passed through a series of mixed bed demineralizers (PE) to be used again as FW.

Understanding this relationship, specific areas of corrosion are identified. Fig. 4 clearly shows how changes in FW Mn mass transport has an effect on the other process streams, and how these data can be used to identify corrosion rates. Using the data from August 31, the following information is obtained. The PE has a Mn mass transport of 100 mg/h, while the HPHD Mn transport is 290 mg/h. Therefore, the FW Mn transport should be 390 mg/h. In actuality, the FW Mn transport rate is 850 mg/h, which indicates a Mn production rate of 460 mg/h.

The second area of corrosion concern is with the HPHD system. Again using the data of August 31, a similar correlation is shown. The MS Mn Mass transport rate of 400 mg/h minus the COND Mn mass transport of 200 mg/h equals 200 mg/h, the calculated value of the HPHD. However, the measured value of 290 mg/h Mn indicates Mn production occurring at the rate of 90 mg/h.

These results may appear relatively low. However, considering the manganese content of carbon steel which may range from 0.6% to 1.0% [19] and correlation constant using the total manganese-to-iron ratio [2], these corrosion rates equate to over 200 pounds of iron per year.

CONCLUSIONS

An improved method for ultra-trace (pg/ml) determination of manganese in power plant waters has been developed. The method uses a selective concentration chemistry, a unique carboxylated ion exchange separation and a sensitive post-column detection for picogram levels of manganese in high concentrations of ammonium matrix. The detection limits of this method were found to be 1 to 3 pg/ml Mn for 80 to 100 ml sample concentration.

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