# Determination of Manganese in Environmental Samples by UV-Vis after Cloud Point Extraction

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*Abstract*—**Cloud point extraction was used with 1-(2-pyridylazo)-2-naphthol (PAN) as a pre-concentration step prior to UV-vis spectrophotometer determination of trace amounts of manganese in water samples. The process is based upon the formation of Mn(II)/PAN complexes soluble in a micellar phase composed by the non-ionic surfactant Triton X-114 (octylphenoxy polyethoxyethanol). Trace Mn(II) /PAN complexes followed by UV-vis spectrophotometer measurement. In this proposed procedure, when above its cloud point temperature, these complexes are then extracted into the surfactant-rich phase. The parameters affecting the extraction efficiency, i.e. pH of aqueous solution, concentration of the PAN, amount of the surfactant, incubation temperature, and incubation time were investigated. The calibration graph was linear in the range 15-500 ng·mL$^{-1}$ with a limit of detection (LOD) of 5 ng·ml$^{-1}$. The proposed method was successfully applied for the determination of trace manganese in various water and soil samples.**

*Keywords-cloud point extraction; manganese; ultraviolet–visible spectroscopy*

## I. INTRODUCTION

Manganese (Mn) is an indispensability for the appropriate function of a few enzymes and a necessary micro-nutrient for the function of the brain, nervous system, and normal bone growth. Enzyme and membrane transport functions are optimized by manganese [1-3]. Mn is a necessary trace element which can be appeared in several food varieties such as tea, grain, rice, soya bean, egg, nut and cereal. Some organisms such as diatoms, mollusca and sponge animal can accumulate manganese element [4]. However, superfluous levels of Mn are harmful to the body, giving rise to poisonousness to central nervous system, respiratory system, and reproductive system. Human who exist in a high concentration of manganese ion in the environment for a long-term can cause interference of mental and emotions and slow, clumsy physical actions [5]. Therefore, it is important to determinate the trace amounts of Mn in various matrices samples for certain areas, such as environmental chemistry and food processing [6].

Determination of the trace amounts Mn in environmental sample or biological sample is very difficult due to many kinds of influence factors. UV-vis spectrophotometry is a useful analytical method for determination trace amounts of elements in environmental matrices sample. However, preconcentration and separation of Mn and iron is still essential, the correlation processing techniques such as liquid-liquid extraction [7], co-precipitation [8], solid-phase extraction [9-11] and cloud point extraction [12].

Separation and preconcentration of cloud point extraction (CPE) are becoming a significant and actual application of surfactants in analytical chemistry [13-15]. Cloud point extraction technology is a new type of liquid-liquid extraction technology [16]. It depends on the solubilization phenomena and cloud point character of surfactant in aqueous solution to take shape micelles and separate two phase. One phase is a surfactant-rich phase of little volume, and another phase is diluted aqueous phase of a large volume when the surfactant solution is heated to a certain temperature so-called cloud point temperature. The hydrophobic compounds originally existing in the sample solution and bound to the micelles are extracted to the surfactant-rich phase. The little volume of surfactant-rich phase of getting from cloud point extraction allows the design of extraction methods that are simple, speedy, cheap, efficient and low toxicity to environment compared with the general liquid-liquid extraction technology. This separation technology has gained a great deal of attention, because the cloud point extraction technology has great potential to separate toxic matrix samples.

In the present work, we study a kind of simple, high sensitivity and high selectivity of cloud point extraction to enrichment of trace amounts of manganese ion in environmental sample matrix and UV-vis spectrophotometry has been used as quantitative assay of manganese ions. An analytical method was established which the PAN as complexing agent and the Triton X-114 as the surfactant. Trace amounts of manganese ion in environmental samples were extracted by the cloud point extraction.

## II. EXPERIMENTAL

### A. Materials and Chemicals

Stock standard solution of 1000 mg·L$^{-1}$ Mn$^{2+}$ was carefully prepared by dissolving MnSO$_4$ in 2% (v/v) HNO$_3$. Working standard solutions were obtained daily by stepwise dilution from standard stock solution with Double Distilled water (DDW). The chelating reagent was prepared by dissolving PAN in CH$_3$CH$_2$OH with a final DDTC concentration of 4×10$^{-3}$ mol·L$^{-1}$. The non-ionic surfactant Triton X-114 purchased from Aladdin was used in this work with a final Triton X-114 concentration of 50 g/L. The desired pH of the solutions was adjusted by using 0.2 mol·L$^{-1}$ NH$_3$·H$_2$O and 0.2 mol·L$^{-1}$ NH$_4$Cl. DDW was used throughout the whole work.

## B. Apparatus

UV2550 ultraviolet and visible spectrophotometer (SHIMADZU) was used for quantitative analysis of manganese. A centrifuge model TDZ5-WS (Shanghai Lu Xiangyi centrifuge Instrument Co., Ltd, Shanghai, China) was used to facilitate phase separation. The pH values were measured by Ohaus Starter 3C pH meter (Pine Brook, NJ, USA).

## C. Samples Preparation

The soil was sampled from the mountain, gardens and fields that located in China West Normal University. The collection of soil used four points sampling method, and then these soil samples were dried at 120 ℃ for up to 24 h until constant dry weight was achieved. Soil sample was grinded with ceramic mortar and pick out chunks of rock and grassroots etc. Then sample was sieved with 100 mesh points. The samples were used for later analysis. Using tools such as mortar and sample points screen etc were washed cleanly with anhydrous ethanol before the sample processing. It can prevent the sample pollution to affect the results of the determination. A 5.0 g dried soil samples was weighted into a plastic tube and 0.1 mol/L HCl solution (1:10, v/v) was added. The resulting mixture was subject to stirring evenly for overnight, followed by keeping in room temperature oscillation for 3 h and filtering. Then, three kinds of the acid leaching soil solutions were used for the subsequent analysis.

## D. Operating Procedure

A certain amount of standard solution of manganese was taken in 10 mL centrifuge tube. Added 0.1 mL of $4×10^{-3}$ mol·L$^{-1}$ PAN solution, 0.8 mL of pH=9 buffer solution and 1.0 mL of 50 g·L$^{-1}$ Triton X-114 solution. DDW was used as to ensure volume 10 mL and shaken well. The solution containing analyte was heated in the water bath at 50℃ for 15 min. Separation of the phases was achieved by centrifugation at 4000 rpm for 10 min. Then, it was cooled in an ice bath for10 min to increase the viscosity of the surfactant-rich phase. The aqueous phases can readily be discarded by inverting the tube. Anhydrous ethanol was added to the surfactant-rich phase (200 μL) to reduce its viscosity and to promote sample treatment prior to UV-vis spectrophotometer. Finally the solution (3 mL) was detected by UV-vis spectrophotometer. Blank solution was also operated a similar procedure and measured in parallel to the sample solutions.

## III. RESULTS AND DISCUSSION

### A. Detection Wavelength

According to the experimental methods after operation, a certain amount of manganese standard working solution was taken and detected absorption spectrum of solution under the UV-vis spectrophotometer. The results are showed in Fig.2 that solution's absorbance value was maximum when the detection wavelength at 553 nm. Therefore, this experiment determined 553 nm as the best detection wavelength.
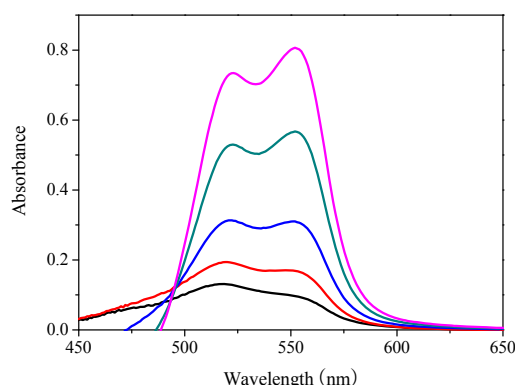


FIGURE I. ABSORPTION SPECTRUM OF MANGANESE STANDARD SOLUTIONS.

### B. Effect of pH

It needs appropriate complexing agent and metal ions to form hydrophobic complex when metal ions are extracted by the cloud point extraction. Then complex is extracted to surfactant phase and extraction rate depends on the acidity of complex formation solution. Therefore, the different pH has an effect on extraction rate of $Mn^{2+}$. Cloud point extraction of $Mn^{2+}$ was carried out in the pH range7-11. The results are shown in Fig. 3. The recovery of $Mn^{2+}$ increased with increasing pH from 7 to 9, and reached a maximum at pH 9.0. Because the manganese and PAN can generated a stable complex in alkaline condition. Under the condition of alkali, it could be a problem for the hydrolysis of $Mn^{2+}$. Taking into consideration of all these factors, pH 9.0 was chosen for use in this work.
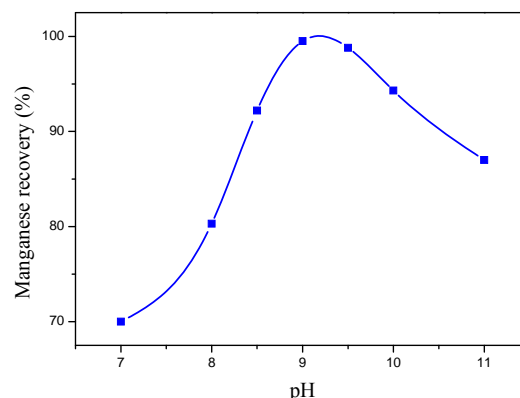


FIGURE II. EFFECT OF PH ON THE CLOUD POINT EXTRACTION OF $MN^{2+}$(100 NG·ML$^{-1}$). EXPERIMENTAL CONDITIONS: 0.5% (V/V) TRITON X-114 AND 4×10-5MOL·L$^{-1}$ PAN.

### C. Volume of the PAN

Chelating agent is one of the key factors influence the extraction efficiency. As shown in Fig. 4, cloud point extraction of $Mn^{2+}$ was carried out in the volume of the PAN range 0.04-0.16 mL. The recovery of $Mn^{2+}$ increased with increasing of PAN volume from 0.04 to 0.10 mL, and reached a maximum at PAN volume 0.10 mL. However, when PAN volume is higher than 0.10 mL, extraction rate declined. It could be excessive free PAN into the surfactant-rich phase and

lead to $Mn^{2+}$ was replaced by PAN, then $Mn^{2+}$ entered into main water phase. Taking into account all these factors, volume of the PAN 0.10 mL was chosen for use in this work.
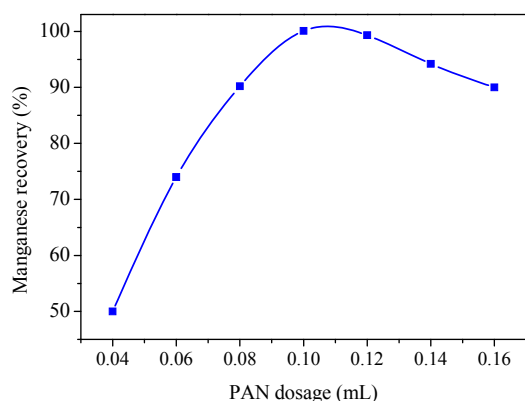


FIGURE III. EXTRACTION EFfiCIENCY OF THE COMPLEX AS A FUNCTION OF VOLUME OF THE PAN. EXPERIMENTAL CONDITIONS: $MN^{2+}$ (100 NG·ML⁻¹), 0.5% (V/V) TRITON X-114 AND PH 9.

### D. Concentration of Triton X-114

Triton X-114 is one of the non-ionic surfactant extensively used in CPE. Because that is its benefits such as commercial availability with high purity, low toxicity and cost, high density of the surfactant-rich phase can promote the phase separation by centrifugation, and relatively low cloud point temperature. As shown in Fig. 5, cloud point extraction of $Mn^{2+}$ was carried out in the Triton X-114 concentration range 0.2-1.0% (v/v). The recovery of $Mn^{2+}$ increased with increasing of Triton X-114 concentration from 0.2% to 0.5%, and reached a maximum at Triton X-114 concentration 0.5%. However, when Triton X-114 concentration is higher than 0.5%, extraction rate was invariant. This showed that the quantity of enough TritonX-114 can ensure the chelate extracted absolutely to ensure the extraction complete and improve the measurement sensitivity. Thus, a concentration of 0.5% (v/v) Triton X-114 was used for subsequent experiments.
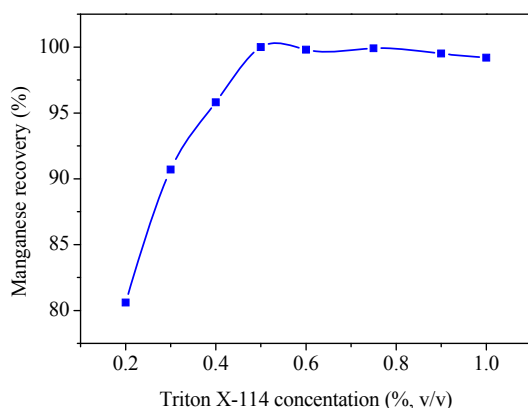


FIGURE IV. EXTRACTION EFfiCIENCY OF THE COMPLEX AS A FUNCTION OF TRITON X-114 CONCENTRATION. EXPERIMENTAL CONDITIONS: $MN^{2+}$ (100 NG·ML⁻¹), $4 \times 10^{-5}$ MOL·L⁻¹ PAN AND PH 9.

### E. Incubation Time and Temperature

In order to get ration extraction, we also investigated other experimental conditions such as incubation temperature and incubation time. It is appropriate to use the shortest incubation time and the lowest incubation temperature probable. The dependency of extraction recovery to the incubation time and temperature was investigated in the range 5-30 min and 30-65 ℃, respectively. The results showed that an equilibration time of 15 min. And 50 ℃ were enough to indicate ration extraction.

### F. Interference Study

The potential interference from co-exist positive ions was carefully studied with 100 ng·mL⁻¹ $Mn^{2+}$ so that it can prove the superior selectivity of the proposed method. The investigation of interferences with the determination of $Mn^{2+}$ arising from other interfering species in the cloud point extraction was tabulated in table 1. These results prove that the general coexisting positive ions did not have a prominent effect on the separation and determination of the $Mn^{2+}$. Therefore, the effects of other ions at given concentrations are ignorable.

TABLE I. INVESTIGATION OF INTERFERENCES FROM CO-EXISTING METAL IONS FOR THE DETERMINATION OF 100 NG·ML⁻¹ $MN^{2+}$ BY USING CPE PRECONCENTRATION FOLLOWED BY UV-VIS SPECTROPHOTOMETER DETERMINATION.

| Iron | Interference/metal ratio | Recovery (%) |
|---|---|---|
| Mg(II) | 1000 | 98.2 |
| Cu(II) | 100 | 99.6 |
| Zn(II) | 10 | 95.5 |
| Pb(II) | 20 | 90.6 |
| Fe(III) | 50 | 98.1 |
| Na(I) | 2000 | 100.1 |
| Ni(II) | 200 | 97.2 |
| Ba(II) | 2000 | 96.7 |
| K(I) | 5000 | 101 |
| Ca(II) | 1000 | 100.3 |

### G. Analytical figures of Merit

Under the optimal conditions, the analytical performance of the proposed method was studied. The calibration graph was linear from 15 to 500ng·mL⁻¹ with a correlation coefficient of 0.9988. The corresponding equation was found to be A =0.00223C+0.001863, where A is the absorbance and C is the manganese concentration in ng·mL⁻¹. The limits of detection (LODs, 3σ) were 5.0 ng·mL⁻¹ for $Mn^{2+}$. Enrichment factor was 35. The precision of (RSD) the CPE procedure was found to be 3.2% for $Mn^{2+}$ (100 ng·mL⁻¹, n = 11).

### H. Application

In order to evaluate the dependability of the method, it was applied for the determination of $Mn^{2+}$ in three natural water samples including river water(Huatan River), river water(Jialing River) and tap water(Xihua normal university). The results (Table2 and Table3) show that the proposed CPE method can be successfully applied for the recovery, pre-concentration and determination of Mn(Ⅱ)in the tested water samples.

TABLE II. DETERMINATION OF MANGANESE IN THE WATER SAMPLES BY THE PROPOSED METHOD.

| Sample | Manganese (ng·mL$^{-1}$) | | | Recovery (%) |
|---|---|---|---|---|
| | Added | Found | R.S.D (%) | |
| Tap water | 0 | 27.5 | 1.5 | - |
| | 100 | 127.7 | 1.7 | 100.2 |
| | 400 | 427.0 | 1.2 | 99.8 |
| River water (Huatan River) | 0 | 48.5 | 1.8 | - |
| | 100 | 148.1 | 1.3 | 99.6 |
| | 400 | 440.9 | 1.6 | 98.1 |
| River water (Jialing Raiver) | 0 | 49.7 | 1.4 | - |
| | 100 | 149.6 | 1.5 | 99.9 |
| | 400 | 454.4 | 1.7 | 101.2 |

TABLE III. DETERMINATION OF MANGANESE IN THE SOIL SAMPLE BY THE PROPOSED METHOD.

| Sample | Manganese (ng·mL$^{-1}$) | | | Recovery (%) |
|---|---|---|---|---|
| | Added | Found | R.S.D (%) | |
| Mountain soil | 0 | 2.944 | 2.8 | - |
| | 100 | 4.906 | 3.1 | 97.7 |
| | 400 | 10.976 | 2.4 | 100.1 |
| Garden soil | 0 | 3.234 | 1.7 | - |
| | 100 | 5.258 | 2.5 | 101.5 |
| | 400 | 11.258 | 2.9 | 99.5 |
| Filed soil | 0 | 3.46 | 3.0 | - |
| | 100 | 5.416 | 2.3 | 100.3 |
| | 400 | 11.398 | 2.8 | 98.6 |

## IV. CONCLUSIONS

The reagent PAN was successfully applied in a CPE procedure for determination of trace amounts of manganese in environmental sample by UV-vis spectrophotometer. This work provides a simple, high sensitivity and high selectivity, and non-polluting technology for the preconcentration and determination of trace manganese metals. Triton X-114 is of relative low-cost and low toxicity. PAN is a very stable and fairly selective complexing reagent. Due to good analytical characteristics, the proposed CPE procedure has been demonstrated to be very interesting for trace manganese iron analysis method.

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