



Indirect Determination of Manganese in Its Slag by Atomic Fluorescence Spectrometry

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A novel method, based on that when the manganese in its slag was enriched and separated by a water soluble polymer, polypropylene pyrrolidone, the standard As(III), which was added, reduced the manganese in a 0.3 mol/L sulfuric acid medium, and the excess As(III) was determined on behalf of manganese, is established for indirect determination of manganese by hydride generation-atomic fluorescence spectrometry. Under optimum conditions, manganese content in 0-16 $\mu\text{g/L}$ showed a good linear relationship. The detection limit was 0.0091 $\mu\text{g/mL}$. The method was applied to determine the manganese in its slag with a satisfactory result.

Keywords: Atomic fluorescence spectrometry, Polypropylene, Indirect determination, Manganese.

INTRODUCTION

The manganese ore resource in Guangxi province is nationwide No. 1. However, the manganese slag produced from majority of its electrolytic industries is 5-6 times of its yield. Most of the slag were piled up in open air and leached by rainwater, resulting in the production of exudates consisting of sulfate, ammonia nitrogen and high concentration of manganese as main pollutants. Manganese is an essential trace element in human being, its deficiency may lead to dwarfness, anemia, asthma, Parkinson disease, mental retardation, tumor, *etc.*^{1,2}. On other hand, excessive level of manganese relates to irreversible brain disease, showing a psychological and neurological disorder, such as manganese poisoning³. Large amount of manganese exposure on environment is the limiting factor on crop growth and main pollution source in human life. Thus, determination of manganese in its slag becomes necessary and significant.

At present, the methods for manganese determination mainly are spectrophotometry⁴, electrochemistry^{4,5}, atomic absorption spectrophotometry^{6,7} and inductively coupled plasma atomic emission spectrometry (ICP-AES). Although ICP-AES can achieve the simultaneous determination of multi-element purpose, its expensiveness limits its application, meanwhile, it is difficult to solve a large number of spectral interference. In atomic absorption spectrophotometry, when the atomization is achieved by sample solution spray, some thermodynamic factors alter, leading to precision deterioration. Considering that atomic fluorescence spectrometric method is better than other methods in some circumstances for its wide linear range, low

detection limit, high precision and strong resistance against matrix interface, the instrument attracts many researchers' attention for determining trace amount of arsenic, mercury, antimony, bismuth, selenium, tellurium, germanium, tin, lead, zinc and cadmium analysis in food hygiene, environmental monitoring, geological, metallurgical and other fields.

Since there has not been manganese hollow cathode lamp commercially available so far for atomic fluorescence, it is not possible to directly determine the element using this technique. However, there may be an alternative approach to measure it by taking the unique advantages of this instrument. Polypropylene pyrrolidone (PVP) is a kind of water soluble polymer material which in certain conditions is able to adsorb some metal ions to form precipitates, achieving enrichment and separation. In this paper, PVP was utilized to preconcentrate the manganese in the sample in advance, then, all manganese in low valance state was oxidized to permanganate which further reacted to the added standard As(III). Thus, the excessive As(III), determined by hydride generation-atomic fluorescence spectrometry, was inversely proportional to permanganate. The method not only is simple and easy to operate, but also extends the scope of atomic fluorescence determination. After the experimental conditions of the determination were explored, the method was submitted to sample, resulting in satisfactory results.

EXPERIMENTAL

The solution was prepared by gradually diluting the manganese standard solution of 1 mg mL⁻¹ procured from National Standard Materials Center (Beijing, China). For

preparation of potassium permanganate standard solution, a certain amount of potassium permanganate was weighed to prepare its stock solution according to the standard preparation procedure and standardized by sodium oxalate; finally the concentration was $1.0050 \text{ mg mL}^{-1}$. Its target concentration was obtained by diluting the stock solution with water. The working solution of arsenic was prepared by gradually diluting the 1 mg mL^{-1} standard arsenic solution purchased from National Standard Materials Center (Beijing, China). Potassium borohydride solution (15 g/L) was prepared by weighing 3 g KBH_4 and dissolved in 200 mL of 5 g/L NaOH , prepared when used. For polypropylene pyrrolidone solution (PVP) (20 %), 20 g polypropylene pyrrolidone were weighed, dissolved in water, transferred into a 100 mL volumetric flask and diluted to mark. Certified standard reference material of multimetal ore (GBW07162) was provided by Beijing Standard Material Center (Beijing, China). Ammonium persulfate, potassium nitrate, sulfuric acid, hydrochloric acid and nitric acid were all analytical grades. The water used in the experiment was double-distilled. All glasswares were soaked in diluted nitric acid overnight for eliminating any contaminants.

The AFS-2202E atomic fluorescence spectrometer (Beijing Haiguang Technology Development Co. LTD, China) equipped with arsenic hollow cathode lamp (General Research Institute for Nonferrous Metals of China) was used to measure the fluorescence intensity emitted from a target element. XS105 Dua Range analytical micro balance (Mettler Toledo, Switzerland) was utilized to obtain sample weight. Instrumental parameters for determining arsenic are listed in Table-1.

TABLE-1
INSTRUMENTAL PARAMETERS FOR ARSENIC

| Parameters | Values |
|--------------------------|-------------|
| Negative high voltage | 280 V |
| Lamp current | 70 mA |
| Atomizer height | 8 mm |
| Flow rate of carrier gas | 400 mL/min |
| Flow rate of shield gas | 1000 mL/min |
| Read time | 14s |
| Delay time | 1s |
| Measurement method | STD |
| Read mode | Peak area |

Sample preparation and digestion: After the manganese slag obtained from a resource was dried naturally. It was ground to powder and sieved through 0.154 mm screen aperture and put in an oven to dry 6 h at $100 \text{ }^\circ\text{C}$. Then the sample was moved in a plastic zip bag and stored in a desiccator for use.

Above sample of 0.5000 g was accurately weighed in a 100 mL beaker and mixed with a small quantity of water. Then 20 mL freshly prepared aqua regia were added. The beaker was covered with a watch glass to prevent the loss of sample and placed on a hot plate with low temperature in a hood for 0.5 h until blown fume appeared. Then, the sample was removed from the plate and cooled to room temperature. After addition of 10 mL sulfuric acid, the beaker was continually heated at low temperature to white fume appearance. After removed from the hot plate and cooled to room temperature, the sample was filtrated into a 100 mL volumetric flask and

diluted to mark. A blank was prepared with the same manner simultaneously.

Experimental method: The digested sample solution of 10 mL was pipetted into a 100 mL beaker and 1 mL NaNO_3 and 0.5 mL polypropylene pyrrolidone solutions were added. The pH of the sample solution was adjusted with NaOH solution of $1 \times 10^{-3} \text{ mol/L}$. After the addition of 30 mL acetone, metal polymer precipitate appeared and underwent centrifugal separation. The supernatant was slowly poured out and the precipitate was dissolved with 10 mL water in a 100 mL beaker. In the beaker 2 mL sulfuric acid (50 %), 1 mL phosphoric acid (50 %) and 0.5 g ammonium per sulfate were added. The solution was boiled for 5 to 10 min , oxidizing the manganese in low valance to MnO_4^- and destroying excessive $\text{S}_2\text{O}_8^{2-}$. Once cooled to room temperature, the solution was transferred into a 25 mL volumetric flask and diluted to mark. At the same time, a blank was prepared in the same manner.

RESULTS AND DISCUSSION

Oxidation conditions of manganese: After 3 mL Mn^{2+} ($10 \text{ } \mu\text{g/mL}$) transferred into a 100 mL beaker, sequentially, 1 mL NaOH and 0.5 mL polypropylene pyrrolidone solution (20 %) were added. The pH of the solution was adjusted to $7-8$ by adding $1 \times 10^{-3} \text{ mol/L}$ NaOH . After the addition of 40 mL acetone, metal polymer started to settle down. After centrifugation, the supernatant was removed, the precipitate was dissolved in water in a 100 mL beaker⁸. Then, 2 mL sulfuric acid (1+1), 1 mL phosphoric acid (1+1) and 0.5 g potassium periodate were added. The solution was boiled and kept warm for 20 min , after the color was completely developed, then removed from the hot plate, cooled to room temperature, transferred into a 50 mL volumetric flask, diluted to the mark with water and mixed thoroughly. Parallel and blank samples were simultaneously prepared. The absorbencies of all the samples were measured by a UV-visible spectrophotometer at wavelength of 525 nm^1 . The absorbed manganese amount was listed in Table-2. It was found that the manganese absorption efficiency of PVP was $98.80-99.76 \%$.

TABLE-2
MANGANESE ADSORPTION ABILITY OF
POLYPROPYLENE PYRROLE (PVP)

| Mn^{2+} added (μg) | Absorbed by PVP ($\mu\text{g/mL}$) | Mn^{2+} (μg) | Absorption (%) |
|--|--------------------------------------|------------------------------------|----------------|
| 30 | 0.5986 | 29.93 | 99.76 |
| 30 | 0.5943 | 29.72 | 99.06 |
| 30 | 0.5927 | 29.64 | 98.80 |

Effect of concentrations of hydrochloric acid in carrier flow and reductant on the fluorescence intensity of arsenic: The production and release efficiencies of the target element hydride would be enhanced when an appropriate acidity of carrier flow was present. It was observed that the fluorescence intensity of arsenic did not change obviously when the concentration of hydrochloric acid was $2-10 \%$. Thus, the effect of concentration of the reductant KBH_4 was investigated. When the acidity of the carrier flow was 5% , the intensity of arsenic showed that the intensity was relatively low when the concentration of reductant was less than 10 g/L . However, when it was higher than 10 g/L , the intensity increased drastically. The

TABLE-3
EFFECT OF COEXISTING IONS

| Ion | K ⁺ | Na ⁺ | Ca ²⁺ | Mg ²⁺ | Cu ²⁺ | Mg ²⁺ | Ba ²⁺ | Al ³⁺ | Cd ²⁺ | Fe ³⁺ | Sn ²⁺ | PO ₄ ³⁻ | SO ₄ ²⁻ |
|------------------|----------------|-----------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|-------------------------------|-------------------------------|
| Tolerance (fold) | 1000 | 1000 | 500 | 1000 | 500 | 1000 | 1000 | 500 | 500 | 25 | 500 | 1000 | 1000 |

sensitivity of the measurement got worse even at higher concentration of reductant. The hydride was diluted with the large quantity of hydrogen gas produced by the reductant. The concentration of 15 g/L yielded a satisfactory result.

Effect of sulfuric concentration on the redox reaction:

The strong oxidation ability of permanganate could be realized in an only acidic medium. In the reaction of MnO₄⁻ and As³⁺, hydrochloric acid should be avoided since it reacted with permanganate; thus, sulfuric acid was used. In order to convert all species of MnO₄⁻ in the solution into Mn²⁺, the stoichiometric ratio between MnO₄⁻ and As³⁺ is at least 3:5 in mass. The variation of sulfuric acid concentration with the arsenic fluorescence intensity was conducted when MnO₄⁻ and As³⁺ were maintained 20 and 50 µg, respectively in the solution. It was found that the As intensity approached stable when sulfuric acid of 3 mol/L existed.

Effect of time on the redox reaction: The reaction time was significant before the equilibrium of MnO₄⁻ and As³⁺ had not reached. The fluorescence intensity was examined within 0.5 h, which showed that the reaction completed in 2 min (Fig. 1).

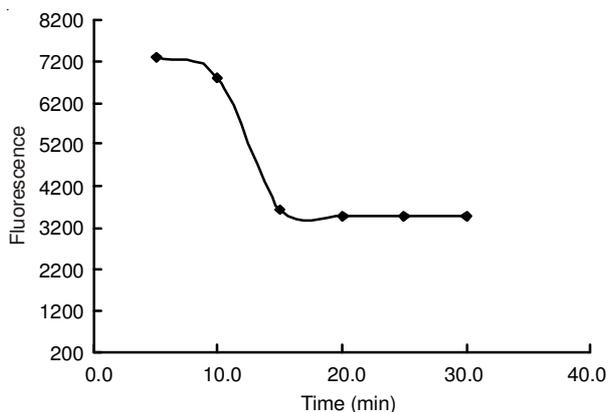


Fig. 1. Effect of reaction time on the fluorescence value of arsenic compound

Interferences: The interference in the experiment was oriented for the ions in the manganese slag sample. When the reaction between 20 µg MnO₄⁻ and 50 µg As³⁺ finished and the relative standard error was kept less than 2 %, the tolerance for the ions was listed in Table-3. As shown in the Table, most of the ions had no interference. However, 25 fold Fe³⁺ yielded interference. Because the high selectivity of PVP, the Fe³⁺ in the sample was excluded and its interference was ignored.

Standard calibration curve and precision: In the optimum experimental conditions, the standard KMnO₄ solution was pipetted into a number of 25 mL colorimetric tubes to prepare a standard series of 0, 2, 4, 8, 10, 12, 16 µg/mL MnO₄⁻. In each tube, 1 mL H₂SO₄ of 3mol/L and 1 mL of standard solution of arsenic (100 µg/mL) were added, and diluted to 10 mL with water. After the series were settled for 20 min, arsenic was determined by atomic fluorescence

spectrometry and found a linear relationship between its concentration and fluorescence intensity in 0-16 µg/mL As with a regression equation of $y = -198.3x + 2123$ and correlation coefficient of 0.9979. The blank including only reagents was determined 11 times, the detection limit 0.0091 µg/mL was calculated based upon $DL = 3 s/S$ (DL: detection limit; s: standard deviation; S: slope of the standard calibration curve).

Determination of manganese slag sample: The samples were digested in accordance with the procedure described and determined under optimum conditions. Meanwhile, the certified standard reference material, polymetallic ore GBW07162(GSO-1) was used to validate the method (Table-4).

TABLE-4
ANALYTICAL RESULTS OF SAMPLES AND RECOVERIES (n = 6)

| Samples | Weigh (g) | Found (µg mL ⁻¹) | | | AVG (µg mL ⁻¹) | Mn (mg g) | RSD (%) |
|----------|-----------|------------------------------|-------|-------|----------------------------|-----------|---------|
| GBW07162 | 0.5000 | 3.89 | 3.86 | 3.85 | 3.87 | 0.89 | 1.6 |
| | | 3.87 | 3.89 | 3.88 | | | |
| Slag A | 0.5002 | 14.52 | 14.54 | 14.49 | 14.51 | 3.35 | 1.9 |
| | | 14.50 | 14.53 | 14.52 | | | |
| Slag B | 0.5003 | 11.49 | 11.47 | 11.53 | 11.49 | 2.65 | 2.1 |
| | | 11.48 | 11.49 | 11.51 | | | |

Conclusion

A simple and sensitive method was developed for the separation and determination of manganese in its slag samples in combination of atomic fluorescence spectrometry. The experimental results showed that the proposed method demonstrated many advantages such as excellent separation, enrichment, simplicity, sensitivity, cost-effective and low consumption of reagents. With high tolerance to co-existing ions and perfect analytical performance, the method proved to be a potential alternative for the determination of manganese in environmental samples.

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