DETERMINATION OF ZINC IN VEHICLE EXHAUST PARTICULATES BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY WITH ELECTROTHERMAL VAPORIZATION

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ABSTRACT

New sample introducing method to ICP-AES is described for the determination of zinc. The impulse graphite furnace of an inert gas fusion was used for the generation of halide vapor (HVG). A 10 μl sample solution of 0.1 mg Zn/ml with 50 mg/ml of ammonium chloride was dropped into the graphite crucible, and vaporized as zinc chloride, heated for 5 second at 2000℃ after dry in 120 second at 100℃. The emission intensity 213.86 nm of zinc was integrated every 0.2 sec. The emission intensity of 1 μg zinc as nitrate and sulfate added ammonium chloride, increased about 100 times. The relative standard deviation by this study was 1.4～4.3 % (n= 6) and the limit of detection was 60 pg (3σ of blank signal). This method was successfully applied to the analysis of a environmental standard reference material (NIES No. 8).

KEYWORDS

Zinc, ammonium chloride, halide vapor generation, graphite furnace ICP-AES, chlorine compound, vehicle exhaust particulates.

1. INTRODUCTION

The graphite furnace atomic absorption analysis that is widely used as a high-sensitivity trace element analysis has two problems: a loss of analyte elements due to evaporation or gasification in the ashing stage before atomization or in the early atomization stage, since the interesting elements are turned to volatile compound under the influence of the coexistent substances; low sensitivity due to the sample penetration into the graphite furnace itself, the carbide generation, etc. In order to prevent these problems, various types of graphite furnace atomizers have been developed [1), 2)]. In addition, from several viewpoints such as separation from the sample matrix and sensitivity improvement, an approach has been developed in which the interesting elements are converted to volatile chemical species[3)-6)]. The study of this paper focuses on the halide vapor generation (HVG) reaction[7)] evaporating and/or volatilizing in a low temperature, which is the problem in the graphite furnace atomic absorption analysis. Using this chemical reaction, the HVG/ICP-AES method was developed for the high sensitivity analysis of zinc by combining the impulse furnace that was used for the inert gas fusion infrared absorption method, with the ICP-AES.

2. EXPERIMENT

2.1 INSTRUMENTS AND APPARATUS

The impulse furnace (hereinafter called the "graphite furnace") of the HORIBA EMGA-520 Oxygen/Nitrogen gas analyzer (inert gas fusion infrared absorption analyzer) was used as a graphite furnace, and HORIBA ULTIMA 2 was used as an ICP-AES. To prevent the plasma blow-off due to incoming atmosphere at the sample entry, the instrument is so configured that the four-way cock is installed at the graphite furnace outlet to switch the cock to the ICP plasma line after the furnace inside was replaced with sufficient argon gas after the furnace is closed. Zinc evaporated and volatilized in the graphite furnace is introduced via Teflon tube (3 mm inner diameter) to the lower section of the torch of ICP-AES of which the nebulizer chamber was removed. Fig. 1 shows the structure and the gas flow of the used graphite furnace. Also, the measuring conditions of the ICP-AES and the temperature condition of the graphite furnace are as follows. Frequency:40.68 MHz, Output power:1.3 kw, Plasma gas:14.0 l/min, Auxiliary gas:2.4 l/min, Carrier gas (Sample gas):0.5 l/min, Carrier support gas:1.0 l/min, Purge gas:1.0 l/min, Observation heigth above coil:15 mm, Integration time:20 sec, Wavelength(Zn):213.86 nm, Dry:120 sec at 100℃, Vaporization:5 sec at 2000℃, Sampling volume:10 μl.

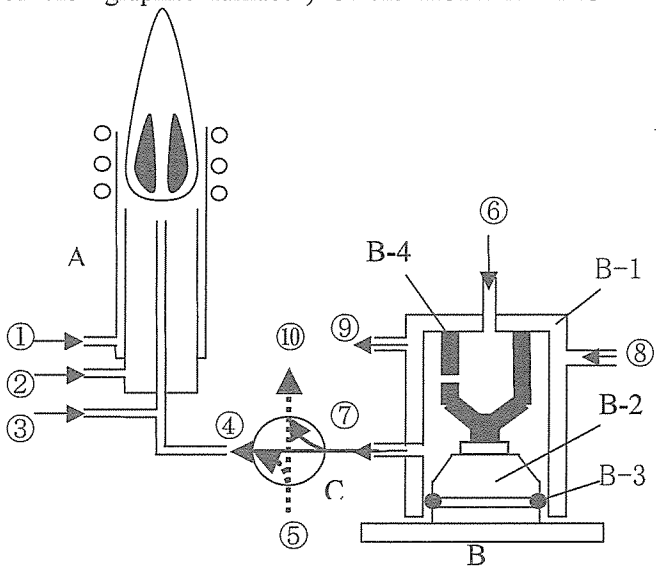

Fig. 1 System for halide vapor generation (HVG) introduction into ICP in combination with electric furnace.
A: ICP-torch, B: Electric furnace, B-1: Upper electrode, B- 2 : Bottom electrode, B-3: O-ring, B-4: Graphite crucible, C: Four-way valve, ①Ar plasma gas inlet, ②Ar auxiliary gas inlet, ③Ar carrier support gas inlet, ④Ar carrier gas outlet to ICP, ⑤Ar purge gas inlet, ⑥Ar carrier gas inlet, ⑦Ar purge and carrier gas outlet, ⑧Water inlet, ⑨Water outlet, ⑩Exhaust.
Argon gas flows: sample drying ⑥→⑦→⑩ / ⑤→④, measurement (heating) ⑥→⑦→④/⑤→⑩.

2.2 Samples and Reagents

Wako Pure Chemical Industries special grade reagents of zinc nitrate (6-hydrate) (99%), zinc chloride (98%), zinc sulfate (7-hydrate) (99.5%), ammonium chloride (99%) and sodium chloride were used. Weight of zinc nitrate (6-hydrate), zinc chloride, and zinc sulfate (7-hydrate) were measured by the electronic balance to produce solutions each with a zinc concentration of 100 mg/ml. These solutions were diluted to produce standard zinc solutions each having a zinc concentration of 0.1 mg/ml. The environment standard sample NIES No. 8 (zinc: 0.104±0.005%) of the National Institute for Environmental Studies was used as a standard sample of automobile emission particles.

2.3 Analysis Operation

The zinc solution of 10 µl with a concentration of 0.1 mg/ml containing ammonium chloride (50 mg/ml) was dropped in the graphite crucible, and then the crucible was placed in the lower electrode (Fig. 1). After the furnace was closed, the 0.15 kW (about 100°C) power was applied for 120 seconds to evaporate water. Then the power was increased to 3.5 kW (about 2,000°C) and kept for

five seconds to evaporate/volatilize zinc in the form of chloride. The generated chloride was introduced to the ICP plasma with the argon carrier gas at a flow rate of 0.5 l/min, and was measured for 20 seconds at every 0.2 seconds to measure the emission intensity of zinc determining the peak area.

3. RESULTS AND DISCUSSION

3.1 Carrier Gas Flow Rate

The emission intensity of zinc has been investigated varying the flow rate of the carrier gas that introduces heated and vaporized zinc in the graphite furnace to plasma from 0.3 to 1.1 l/min. In the range of argon gas flow rates between 0.45 and 0.60 l/min, almost constant high emission intensity were obtained. When the flow rate was lower than 0.45 l/min, the emission intensity was low. This was considered because the vaporized zinc was absorbed inside the furnace and on the inner wall of the pipes on the way of to plasma to a large extent. As a result, the optimum carrier gas flow rate of 0.50 l/min was used.

3.2 Vaporization Temperature and Time

The optimum zinc vaporization temperature was investigated using solutions of zinc chloride, zinc nitrate and zinc sulfate (Zn: each 0.1 mg/ml). The results are shown in Fig. 2. Almost no peaks were detected at 1,000°C or less for zinc nitrate and zinc sulfate solutions. Also, the very low emission intensity were obtained at 2,000°C or more. The reason for this is presumably as follows: the emission intensity were low because both zinc nitrate and zinc sulfate formed zinc oxides having high melting points and consequently, the evaporation/vaporization were insufficient. On the other hand, for the zinc chloride solution, vaporization apparently tends to occur even at a low temperature because the peak was detected even at temperatures 500°C or less. At temperatures of 1,700°C or higher, the emission intensity of zinc became constant, being about a half of the emission intensity at 600°C. When the plasma output was increased from 1.0 kW to 1.3 kW to improve the excitation efficiency, the emission

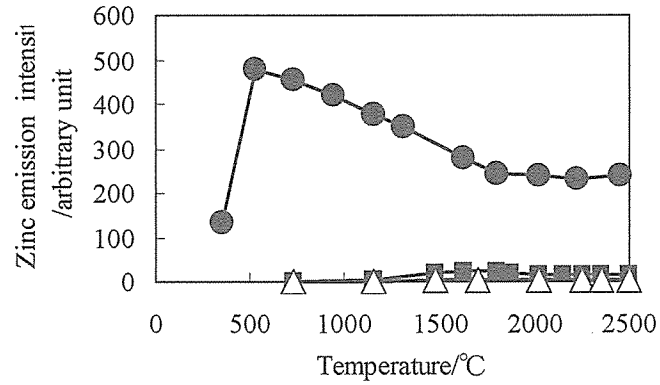

Fig. 2 Effect of the vaporization temperature of the graphite furnace on the zinc emission intensity form various zinc compounds (0.1 mg Zn/ml without the addition of NH_4Cl).
●: $ZnCl_2$, ■: $Zn(NO_3)_2$, △: $ZnSO_4$.

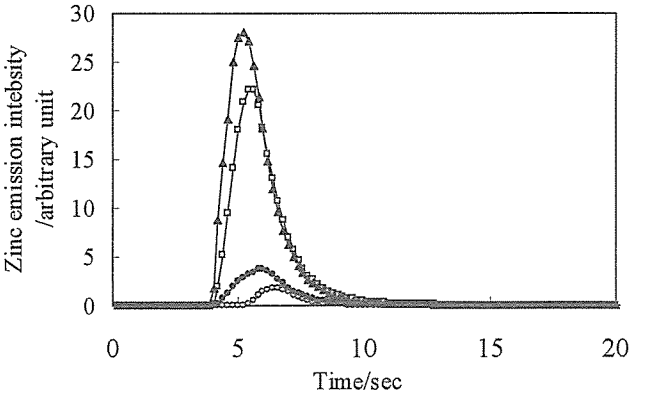

Fig. 3 Zinc emission profiles from zinc nitrate by addition of various chloride compounds.
○: None, □: NH_4Cl (50 mg/ml), ▲: HCl (50 mg/ml), ●: NaCl (50 mg/ml), Drying temperature: 100℃, Vaporization temperature: 2000℃, Sample: 0.1 mg Zn/ml.

intensity of zinc increased about 1.5 times. As a result, it was determined that the optimum vaporization temperature of zinc chloride was about 2,000°C and the plasma output of 1.3 kW was used. In addition, it was determined that the drying temperature was set at 0.15 kW (about 100°C) because the chloride evaporation/vaporization started at 0.35 kW (about 200°C) and in order to prevent the sample from being splashed due to rapid water evaporation. The optimum drying time was determined at 120 seconds because the baseline fluctuation increased at 100 seconds or less.

3.3 Chloride Addition Effect

Chemical modifiers were studied to suppress oxides generation and to efficiently produce chlorides in the form that allows easy vaporization. Emission intensity was investigated when ammonium chloride, hydrochloric acid and sodium chloride that were considered to easily generate zinc chlorides were added (50 mg/ml) to sample solutions having a zinc concentration of each 0.1 mg/ml. Typical examples of the emission intensity profiles are shown in Fig. 3 when the chemical modifiers are added to the zinc nitrate. As a result, the ammonium chloride was determined to use as the chemical modifier since it was considered to be optimum to produce zinc chlorides in any samples.

3.4 Addition Amount of Ammonium Chloride

The sensitivity enhancement effect was investigated by adding the ammonium chloride in the concentration range between 0.005 and 50 mg/ml to the solution having a zinc concentration of 0.1 mg/ml. The results are shown in Fig. 4. The zinc sulfate is considered to hardly become chloride with a small amount of ammonium chloride. However, emission intensity of each sample were the same when the addition amount of ammonium chloride was 50 mg/ml. When the addition amount was 100 mg/ml or more, excess ammonium chloride evaporated/volatilized became white substances and adhered inside the furnace resulting in poor repeatability. Based on this result, the optimum addition amount of ammonium chloride was determined at 50 mg/ml in the following experiments.

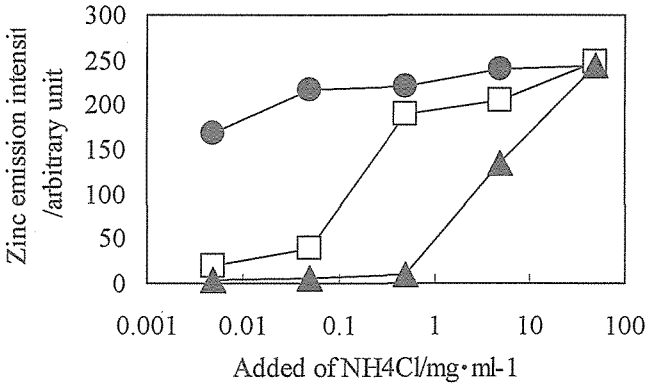

Fig. 4 Effect of the amount of ammonium chloride on the zinc emission intensity from various zinc compounds (0.1 mg Zn/ml).
●: $ZnCl_2$, □: $Zn(NO_3)_2$, ▲: $ZnSO_4$

3.5 Linearity of Calibration Curve and Detection Limit

By adding the ammonium chloride, the calibration curve of good linearity was obtained. The correlation coefficient was 0.999 in the zinc amount range between 5 and 100 mg/l of zinc chloride. The repeatability of 5 mg/l zinc solution prepared using zinc chloride was 3.3%. The detection limit (three times the standard deviation of the blank signal) was about 60 pg, the ammonium chloride solution (50 mg/ml) being the blank. An analysis took about three minutes. The same graphite crucible could be repeatedly used up to about 200 times.

3.6 Influence of Coexistent Elements

To apply this method for analyzing zinc in automobile emission particles, the influence of coexistent elements (aluminum, iron, calcium, sodium, potassium, and magnesium) contained in percent order in automobile emission particles was studied. Coexistent elements of 10, 50, and 100 times the zinc amount were added and their emission intensity were compared to that of zinc without additive. No influence of coexistent elements was recognized for each element up to 50 times the zinc concentration whereas presence of aluminum, calcium and magnesium with concentrations 100 times the zinc concentration resulted in lower emission intensity than that of zinc without additive. For the sodium and potassium, the emission intensity was measured high.

3.7 Real Sample Analysis

As the standard samples of automobile emission particles, the environment standard sample NIES No.8 and the particulate matter of which zinc concentration was unknown were used. The latter was taken from the inner wall of the automobile emission gas dilution tunnel. As the result of measurement on the dissolved solution from the automobile emission particles in accordance with this method, the average of three times NIES No. 8 measurements was $0.103 \pm 0.005\%$, which matched with the certified value ($0.104 \pm 0.005\%$). The measurement on the particulate matter of the inner wall of the dilution tunnel indicated $0.045 \pm 0.004\%$.

4. CONCLUSIONS

The impulse furnace of the inert gas fusion infrared absorption method used in the field of iron and steel analysis was newly combined with the ICP-AES to establish the HVG/ICP-AES method based on halide vapor generation, in which ammonium chloride (50 mg/ml) was added as a chemical modifier to convert zinc into zinc chloride that is easy to vaporize. A hundred fold increase in sensitivity was obtained for zinc nitrate and zinc sulfate. The repeatability of this method was between 1.4 and 4.3% ($n = 6$) in relative standard deviation. The detection limit (three times the standard deviation of the blank signal) was about 60 pg. When this method was applied to an analysis of zinc in automobile emission particles, it was confirmed that the measurement was possible without influence of coexistent elements.

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