広島大学学位請求論文

Development of rapid and high sensitive analytical methods based on electrothermal vaporization - inductively coupled plasma atomic emission spectrometry for impurities in fine particles

（電気加熱気化－高周波誘導結合プラズマ原子発光分光法による微粒子中不純物の迅速・高感度定量法の開発）

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広島大学大学院理学研究科

化学専攻

中田　健一

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(1) Determination of thallium by heated quartz cell atomic absorption spectrometry with tungsten boat furnace vaporizer, Yasuaki Okamoto, Kenichi Nakata, Terufumi Fujiwara, and Takahiro Kumamaru, *Analytical Sciences*, **13**, 299-301 (1997).

主論文

Development of rapid and high sensitive analytical methods based on electrothermal vaporization - inductively coupled plasma atomic emission spectrometry for impurities in fine particles

Kenichi Nakata

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Chapter 1

General Introduction

The progression of the research concerning nanotechnology was set the stage by the statement of Dr. William Jefferson Clinton, the then President of the United States, about the adoption of Nanotechnology National Strategy Declaration of 2000. Thereafter, nanotechnology attracted immediate worldwide attention as one of the most important modern technological fields. Consequently, nanomaterials themselves and their numerous applications or usage have been developed in the field such as electronic and optical devices, cosmetics, medicines, ceramics, and so on.

Dry and wet process has been studied to prepare conductive nanoparticles such as silver nanoparticles in industrially manufacturing processes [1]. Regarding silver nanoparticles, they are essential materials in the ink jet and screen printing processes to manufacture various electric circuits, because of their good dispersibility and sintering characteristics at low temperatures [2,3,4]. However, several problems have also emerged with increasing the use of these nanomaterials. One of the most serious problems is that, nanoparticles produced by liquid-phase preparation often contain some impurities which located on the particle surfaces as well as inside of the particles, and that the impurities affect the characteristics of the particles [5]. For example, the presence of some silicate on fine iron oxide particles changes the electrostatic charge of their surface, which affects the absorption properties of myristic acid [6]. This phenomenon is also observed in other fine particles and lead to the dispersibility change in a solvent. Because nanoparticles have large surface area with high reactivity, the impurities should not be neglected. When there is a sulfur or chlorine atom as impurities in an electric circuit, metal parts of the end product tend to corrode earlier. As the results, the breakdown of the end product will be occurred before its design life. Manufacturing methods in various industrial-scales have been developed to avoid these issues caused by the presence of impurities. Impurities such as sulfur and chlorine can be reduced by using silver oxide or silver carbonate as raw materials with the use of organic protecting agents [7]; the use of a dry manufacturing process with an electric beam also prevents contaminations into nanoparticles [8]; in addition, washing of nanoparticles repeatedly with a polar solvent also reduces the contamination [9]. Needless to say, it is very important to control the quality of raw materials and products by reducing the contamination not only caused during their production but also caused by the environment during storage. Sulphidizing might be considered because there are many active volcano in Japan.

To evaluate the trace impurities in metallic materials using inductively coupled plasma atomic emission spectrometry (ICP-AES), the sample solution must be prepared by dissolving the sample material in acids such as nitric acid; the resulting solution is then subjected to ICP by using the nebulizer. However, acid digestion will decrease the sensitivity because of the dilution of the analyte with water and will decrease the excitation efficiency of the analytes with decreasing the plasma temperature by the accompanying water mist. If the analytes are the elements such as silicon or chlorine, then sedimentation of silicic acid and volatilization of chlorine occur during nitric acid digestion. Moreover, this preparation is time-consuming and often cause contaminations of the impurities during operation.

Direct solid sampling is an attractive sample introduction technique, wherein solid samples are introduced directly into the ICP spectrometer without any pretreatment. The technique provides the following advantages over conventional nebulization: increased transport efficiency, small sample size, no dilution during sample dissolution, and no contamination during sample preparation. Furthermore, an electrothermal vaporization (ETV) technique with ICP atomic spectrometry allows the selective vaporization of the analyte. That is, in this method, volatile solvents are expelled from the furnace, and the nonvolatile matrix is retained in the furnace during the selective introduction of the analyte into the plasma. This results in the effective excitation of the analyte and leads to the sensitive determination, especially of non-metal elements.

In this research, the direct determination of nonmetallic elements such as silicon, sulfur, phosphorus, and chlorine in nano/fine particles using ETV-ICP-AES was investigated. The determination of silicon, sulfur, and phosphorus in silver nanoparticles has been investigated in Chapter 2, while chlorine in several types of fine particles has also been studied in Chapter 3.

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Chapter 2

Spectrometric estimation of sample amount in aliquot for a direct solid sampling system and its application to the determination of trace impurities in silver nanoparticles by electrothermal vaporization-inductively coupled plasma atomic emission spectrometry

2-1. Summary

A method based on a tungsten boat furnace vaporiser, tungsten sample cuvettes, and an inductively coupled plasma atomic emission spectrometer has been developed for the direct determination of silicon, phosphorus, and sulphur in silver nanoparticles. The important point in the proposed method is that the entire sample in each batch is vaporised, which enables simultaneous measurement of the emission of not only the analyte but also the silver matrix. Furthermore, since the silver nanoparticles are sufficiently pure, the contribution of impurities to the sample amounts will be negligible. Therefore, this estimation is suitable for measuring the sample amount in each aliquot instead of the conventional weighing procedure using a microbalance; therefore, no tedious weighing procedures for estimating the sample amount introduced into the electrothermal vaporization device are needed. An additional advantage is that pretreatment and/or predigestion are unnecessary. The sample throughput is approximately 35 batches per hour. The detection limits of silicon, phosphorus, and sulphur in the silver nanoparticles (dry powder) are 15, 4.2, and 62 μg g^{-1}, respectively. Analytical results for various silver nanoparticles as both dry particles and in suspended solutions are described, and these values are compared to those obtained by conventional weighing with a microbalance. This methodology is useful for rapid screening and accurate analysis of silver nanoparticles, especially for industrial applications.

2-2. Introduction

As membrane wiring boards and flexible printed circuits have increasingly been developed and fabricated, electronic applications, especially for domestic use, have become progressively sophisticated. Among electronic parts, transparent electrodes are essential components because they are used daily in the touch panels of smart and cellular phones, LED screens and plasma display panels, solar cell electrodes, and, recently, wearable computers; in addition, there are a variety of future applications. These transparent electrodes are sometimes produced by painting a gel-ink or a paste of a certain conductive material on transparent, flexible sheets. During aging of the sheets, the nanoparticles aggregate to form numerous narrow wires, similar to knitting. Light transmits through the many openings among the wires. The conductive materials are prepared by suspending nanoparticles in aqueous or organic solvents. Gold, silver, copper, iron, nickel, etc., and their alloys are used as the nanoparticles. Gold and platinum have excellent durabilities, although they are also the most expensive. Hence, they have been applied primarily in biological and medical areas, where the research can be performed using a small amount of nanoparticles. Copper particles can be purchased at lower prices; however, they are not as durable. Silver particles have a higher durability and are more cost-effective than other metals. Therefore, in industry, silver nanoparticles have been applied comprehensively. In the industrial process for producing silver nanoparticles, there are impurities, which negatively influence the quality of the final products by affecting the dispersibility, printing properties, and storage stability in the liquidised suspended solution form; these impurities include sulphur, silicon, and phosphorus. Even in the metallic solid form, the conductivity of the silver nanoparticles is seriously affected by impurities, and the influence of the impurities is often observed at very low concentrations. For example, the dispersibility deteriorates with increasing concentration of silicon even when sufficient amounts of surfactant are present as a dispersing agent. Fig. 1 shows silver nanoparticles containing silicon are precipitated during the centrifugal liquid sedimentation. As the results, the liquids become transparency. Without silicon, it is difficult to precipitate. Sulphur pollution of raw materials can also impede the electronic conductivity of the final products or transparent electrodes (Fig.2).

The development of a rapid and facile analytical method for the determination of impurities in silver nanoparticles as industrial materials is necessary. For determining these impurities in silver nanoparticles, inductively coupled plasma atomic emission spectrometry (ICP-AES) is a powerful tool from the perspective of satisfactory stability, good repeatability, wide calibration range, and sufficient sensitivity. Depending on the analyte impurities, e.g. metallic elements, it is considered feasible that the silver nanoparticles could be dissolved in nitric acid and then analysed for impurities with nebuliser ICP-AES. However, for the determination of silicon, phosphorus, and sulphur, there is a risk that the silicon impurities will precipitate as silicic acid under such strongly acidic conditions during the final digest. Sulphur and phosphorus often evaporate during vigorous digestion procedures. Moreover, the digestion procedures are usually tedious, time-consuming, and besides, the analytes tend to be contaminated by the laboratory conditions. For sample introduction, although pneumatic nebulisation has been widely applied, direct solid sample introduction schemes are attractive from the viewpoint of analysing only small amounts (several milligrams) of samples, avoiding the contamination inherent to sample preparation procedures, and reducing the time required by avoiding dissolution, dilution, and filling steps. Moore et al. and Sarah et al. applied the laser ablation technique to the direct analysis of ancient or antique silver products [1,2]. An alternate direct introduction technique for solid samples into ICP, i.e. the electrothermal vaporisation (ETV) sample introduction technique, is applicable to solid samples as well as liquid or suspended solutions. Moore and co-workers [3] reported a unique ETV technique based on one-particle sampling followed by *in situ* digestion with nitric acid in a graphite tube furnace. According to their paper, the matrix silver and almost all the analytes dissolved completely to form their nitrate salts, with impurities, such as tin, precipitating in the furnace. The concept was that, regardless of their solubility, all the elements were converted to a species that was suitable for electrothermal vaporisation. In the case of silver nanoparticles, the sample diameter is too small and too little sample is required to accurately and reproducibly weigh aliquots of the particles and place them into the furnace. If the silver nanoparticles were suspended in aqueous or organic solvent in the presence of a suitable surfactant via ultrasonication, the particles would precipitate rapidly because of their high density relative to the solvent. Indeed only several seconds are sufficient for sedimentation. Even if a stable suspension were prepared, the particles would be too hydrophobic to pipette and inject them accurately without some remaining inside the wall of the pipette. With respect to the practicality, there are some handicaps regarding the operation of the ETV-ICP-AES, i.e. estimation of the amount of silver nanoparticles, quantitative introduction of the particles into the ETV device, and the tedious removal of residues if necessary. In particular, estimating the amount of each aliquot taken is the most significant problem in solid sampling ETV because dividing the amount of impurities by the weight of aliquot is necessary to calculate the concentration. When the applied amounts are in the range of several tens of milligrams to sub-gram, the samples can be easily weighed via the usual microbalance procedure by using an exchangeable sample cuvette-tungsten boat furnace system [4]. However, when each aliquot is only several milligrams, the weighing procedure is difficult because of the insufficient sensitivity of the microbalance.

Since the original ICP-AES method is used for the determination of ultratrace impurities, ICP-AES incorporating an ETV device enables further detectability. Therefore, the method is not generally suitable for the quantification of major components. By utilising a wavelength with poorer sensitivity, however, the dynamic range for calibration can be expanded to higher concentrations. In this research, the entire sample in each batch is vaporised for introduction into the ICP emission source, and both the emission intensities of the analyte and matrix silver are measured simultaneously at their respective wavelengths using a spectrometer incorporated two independent monochromators. That is, in order to measure the sample amount in each batch, a spectrometric estimation was applied instead of the conventional weighing method involving a microbalance; concurrently, the analyte impurities are determined by the other monochrometor.

With respect to nanoparticles, significant attention is devoted to counting individual nanoparticles in environmental samples to evaluate pollution by metal particles. To the best of our knowledge, the trace determination of silicon, phosphorus, and sulphur impurities in silver nanoparticles has not been reported to date. There are only reports regarding the determination of free Ag^+ ions as an impurity in a silver nanoparticle solution by fluorescence spectrometry [5] and ICP mass spectrometry (MS) [6]. A direct solid sampling scheme was applied to the determination of silver nanoparticles themselves in botanical samples by high-resolution continuum source GF-AAS [7]. Buchbinder et al. reported the application of a separate sampling and excitation accessory for ICP-AES for the direct analysis of silver ingot [8]. Yang et al. developed a method to isolate trace metal impurities from a silver matrix using selective precipitation followed by ICP-MS [9] and neutron activation analysis [10]. However, although there is potential for the determination of silicon, phosphorus, and sulphur using these methods, no data concerning these elements were reported. Regarding the determination of silicon, phosphorus, and sulphur, Jiang and co-worker reported the determination of these elements in steel samples using ICP-MS [11]. However, silver samples were not investigated.

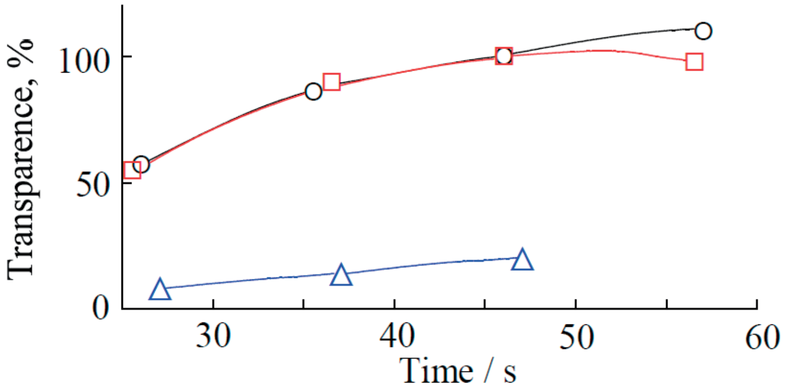

Fig. 1. Effect of transparency on the centrifuge time

○, □, Silver nanoparticles containing ca. 1.7 mg g^{-1} silicon as a impurity;

△, silver nanoparticles without silicon.

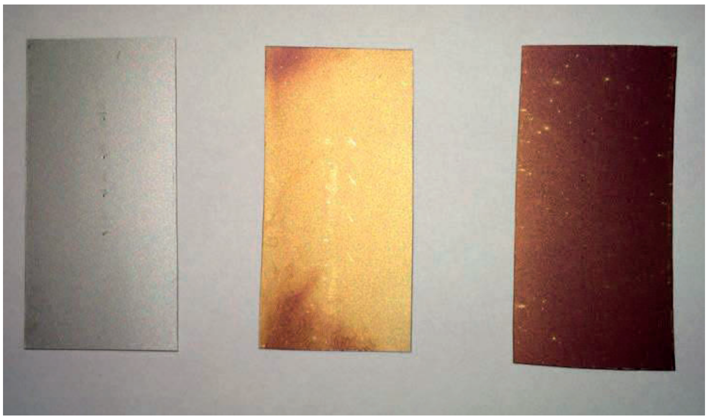

Fig. 2. Photographs of a series of PET films coated by silver nanoparticles

The three photographs are polyethylene-terephthalate (PET) film printed by the paste of silver nanoparticles. The coating thickness is approximately 10 micrometre. With increasing the deterioration by sulphur, the surface resistance increased.

A, Before weatherability test. Since the silver isn't deteriorated by the pollution of sulphur, the surface color is silvery white

and the surface resistance exhibits 0.30 Ω/sq.

B. After medium weatherability test. The surface resistance exhibits 0.34 Ω/sq. The color changes to yellow-brown.

C. After heavy weatherability test. The surface resistance exhibits 0.50 Ω/sq. The color changes to dark-brown.

2-3. Materials and Methods

2-3-1. Reagents

Water from an Advantec Toyo (Tokyo, Japan) Model GSU-601 water purification system was used. All chemicals were commercially available and of analytical reagent grade. Stock standard solutions (1000 mg L^{-1}) of sulphur and phosphorus were prepared by dissolving potassium sulphate and anhydrous potassium dihydrogenphosphate, respectively, in water. Working solutions were freshly prepared by diluting appropriate aliquots of the stock solutions or previously diluted solutions with water. Stock solutions containing 10000 and 1000 mg L^{-1} silver(I) were purchased from Hayashi Pure Chemical (Osaka, Japan). Standard silicon(IV) solutions with concentrations of 10 and 100 mg L^{-1} were purchased from Hayashi Pure Chemical and used as received with no further dilution. Small circular silver pieces were prepared by cutting highly purified silver thin plate (0.01 mm thickness, 99.98%, Nilaco, Tokyo, Japan) into circles with diameters of 0.8 mm and masses of approximately 60 mg.

2-3-2. Silver nanoparticles

Some dry particles of silver nanoparticles were purchased. Other silver nanoparticles were prepared according to the literature [12]. Briefly, into a litre aliquot of 10% silver nitrate aqueous solution containing 3.6 g of Disperbyk-190 (BYK Japan, Tokyo, Japan) as a dispersing agent, 750 mL of an aqueous solution containing 170 g of 2-(dimethylamino)-ethanol and 8.6 g of heptanoic acid was added dropwise overnight at 35°C or colder. Then, the temperature was maintained at 70°C for 3 h for aging. After decantation, the obtained silver nanoparticles were washed with water to remove any soluble raw materials and then lyophilised. To prepare suspension samples, the dry samples were suspended in toluene with a surfactant, such as triton X-100 (Sigma-Aldrich Japan, Tokyo, Japan) under ultrasonication. The resulting concentrations of the suspension samples were ~1000 mg L^{-1}. To evaluate sulphur in silver nanoparticles, silver was sulfureted by treating with sodium thiosulphate solution as required.

2-3-3. Apparatus

A Seiko II (Chiba, Japan) Model SPS4000 ICP atomic emission spectrometer was used. The spectrometer incorporated two radial-view monochromators, by which the emission intensities of two analyte elements could be simultaneously measured at their respective wavelengths. The background emission was corrected for using an oscillating quartz refractor plate that was equipped onto the spectrometer. The pressure inside the spectrometer housing was maintained at 50 Pa or lower by evacuation with a rotary vacuum pump throughout the analysis. The optical path between the plasma discharge and entrance quartz window of the spectrometer was purged with an 8.0 L $\min^{-1}$ nitrogen gas stream during the vaporisation stage. For electrothermal sample introduction, a Seiko II Model SAS-705 ETV device equipped with a tungsten boat (large U-type, 10 mm × 60 mm) was used. If necessary, up to 100 μL of aqueous sample solution and reagent solution could be placed into the furnace. The vaporiser is described in detail in the literature [4,13]. A PTFE tube (4 mm i.d. × 50 cm long) was used to connect the ICP torch of the spectrometer with the inlet port of the vaporiser. The transient emission data were obtained by means of a personal computer attached to the spectrometer. The vaporiser and experimental procedure are illustrated in Fig. 3. A Mettler Toledo (Zurich, Switzerland) Model Xp26 microbalance (readability, 1 μg) was used to weigh the samples of the silver nanoparticles. Gilson Medical Electronics (Villers-le-Bel) Pipetman P-20 and Microman M-25 digital pipettes were used to inject the standard and reagent solutions, respectively.

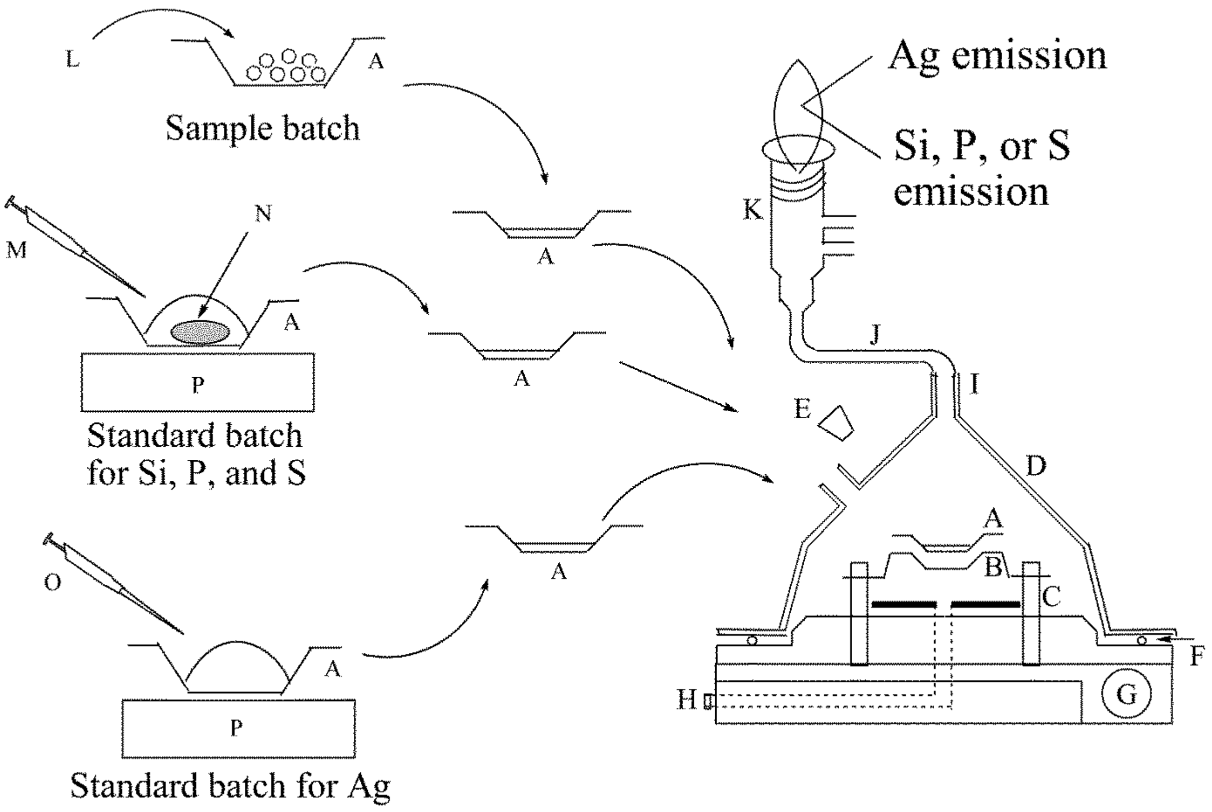

Fig. 3. Schematic diagram of the apparatus and experimental procedure for the direct analysis of silver nanoparticles:

A, sample cuvette made of tungsten; B, tungsten boat furnace; C, furnace electrode; D, glass dome; E, sample cuvette insertion port and silicone rubber stopper; F, O-ring; G, electric terminal; H, carrier-gas inlet port; I, outlet port to ICP; J, Teflon tube; K, ICP torch; L, sample aliquot of silver nanoparticles (dry solid or suspended solution); M, digital pipette for Si, P, or S standard solution; N, silver thin plate; O, digital pipette for Ag standard solution; P, hot plate kept at 110°C.

2-3-4. Recommended procedure

Sample cuvettes were preconditioned by heating to expel silver, silicon, phosphorus, sulphur, and other impurities, and the blank signal levels for the cuvettes were confirmed. For routine analysis of silver nanoparticles in a dry powder form, aliquots of the silver nanoparticles (up to approximately 0.1 mg) were weighed accurately into sample cuvettes; because this weighing is to compare between the conventional and proposed methods, this procedure can be skipped during routine work. For the suspended solutions of particles, aliquots of several tens of microliters of the solution were pipetted from a glass vial under ultrasonication into cuvettes.

To construct calibration curves for silicon, phosphorus, and sulphur, samples were prepared as follows: A highly purified silver plate was placed in the sample cuvette, and an aliquot of the standard solution was pipetted into the cuvette using the digital micropipette. For the evaluation of silver, aliquots of the silver(I) standard solution were pipetted into the empty sample cuvettes. These cuvettes were dried on a hot plate at 110°C prior to the measurement.

One of the sample cuvettes was loaded onto the tungsten boat furnace (TBF) vaporiser. After the insertion port was closed with a stopper, the heating program of the vaporiser was started to induce vaporisation and introduce the entire sample together with the analyte of interest. Argon gas with 15% hydrogen gas was flowed through the vaporisation chamber at a rate of 1.0 L min^{-1} to carry the vapour into the plasma. The emission signals at the wavelengths of both the matrix silver and analyte of interest were simultaneously recorded. The integrated signals (peak areas) were estimated after each vaporisation. Table 1 lists the recommended operating conditions.

Table 1. Instrument operating conditions for analysis of silver nanoparticles

ICP atomic emission spectrometer (SII SPS4000)	
R. F. power	1.5kW
Argon gas flow rate	
Plasma	16 L min^{-1}
Auxiliary	1.0 L min^{-1}
Analytical line	Ag I 211.383 nm
	Si I 212.412 nm
	P I 213.618 nm
	S I 180.734 nm
Observation height	14 mm above load coil
Tungsten boat furnace vaporizer (SII SAS-705V)	
Sample amount	up to 0.1 mg
Drying	200ºC for 35 s (ramp 10 s)
Ashing	500ºC for 10 s (ramp 10 s) for Si
	300ºC for 10 s (ramp 10 s) for P and S
Vaporization	2400ºC for 15 s (ramp 3 s) for Si
	2300ºC for 15 s (ramp 8 s) for P and S
Carrier gas flow rate	
Argon gas	850 mL min^{-1}
Hydrogen gas	150 mL min^{-1}
Purge gas for optical path	
Nitrogen gas	8.0 L min^{-1}
Purge time	18 - 23 s (during vaporization stage)

2-3-5. Calculations

The calculations of the analyte concentration were based on previous paper [14], as per the following equation:

Analyte concentration = (amount of analyte) / (amount of sample) (1)

Normally, the amount of analyte in each aliquot is determined using a highly sensitive analytical instrument, and the amount of net sample is weighed using a microbalance. In the analysis of silver nanoparticles, the numerator is the amount of silicon, phosphorus, or sulphur determined using the ICP atomic emission spectrometer, and the denominator is the amount of silver nanoparticles measured using a microbalance and ICP spectrometer in the conventional and proposed methods, respectively. Since silver nanoparticles exhibit sufficiently high purity, the contribution to the sample amount from the components besides silver will be negligible. Therefore, it is expected that both the amounts measured by conventional weighing and the proposed spectrometric estimation will be equivalent.

2-4. Results and discussion

2-4-1. Optimisation of procedure

Effect of temperature program

Moderate elevation of the temperature throughout the heating process was essential. The temperature and duration of the drying stage were 200°C and 30 s, respectively. In the second stage of the ashing process, the temperature was set at 300–500°C for 10 s. In case organic surfactants are adsorbed onto the surfaces of the silver nanoparticles, the surfactants will be decomposed during the second stage of the ashing process. Figure 4 shows the effect of the vaporisation temperature on silicon, phosphorus, and sulphur in the silver nanoparticles. Regarding the vaporisation temperature of silver, maximum and constant emission intensities were observed within the temperature range of 2000–2800°C. When phosphorus and/or sulphur coexists with silver, thermal stabilities of these elements improves at ashing stage to makes chemical compounds with silver. It was found that silver worked as the chemical modifier to evaporate phosphorus and/or sulphur at vaporization stage. The vaporisation temperatures for silicon, phosphorus, and sulphur were 2400°C, 2300°C, and 2300°C, respectively. The effect of the ramp time for the vaporisation temperature on the sensitivities of the analytes was investigated. To achieve maximum atomic emission signals, the ramp times were set as given in Table 1 for the respective analytes. Hydrogen gas was necessary to prevent deterioration of the TBF and sample cuvettes. The hydrogen gas (150 mL min^{-1}) was admitted through the argon carrier gas flow (850 mL min^{-1}).

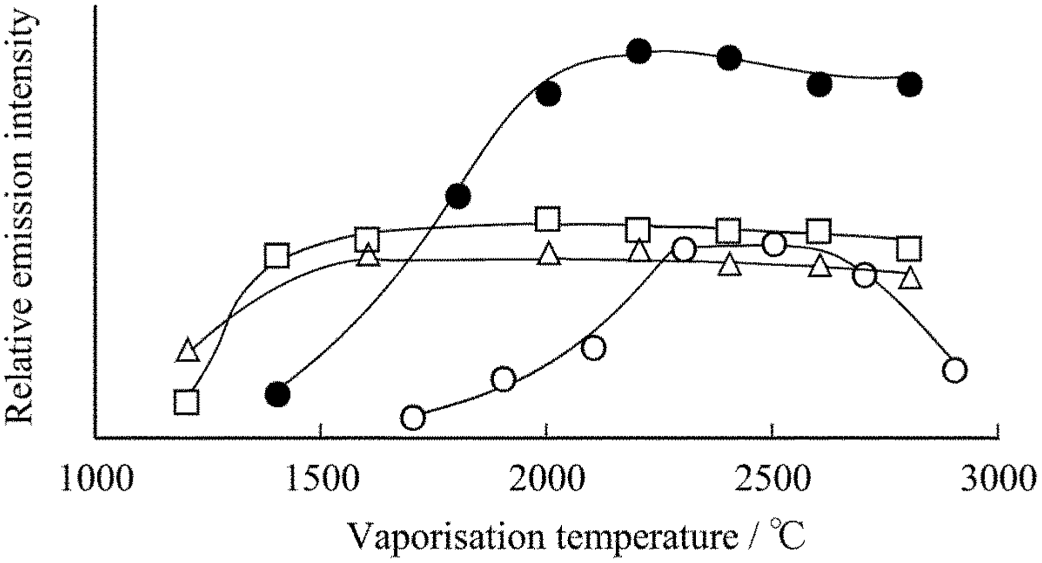

Fig. 4. Effect of vaporisation temperature on the emission intensities of silver, silicon, sulphur, and phosphorus: ●, 2 mg of silver; ○, 160 ng of silicon; □, 20 ng of sulphur; △, 100 ng of phosphorus.

Evaluation of standards

There are remarkable differences in the matrixes of the solid and liquid forms, and external calibration with an aqueous standard solution, which is commonly used in ICP atomic spectrometry, is not possible. Therefore, a calibration curve constructed with solid standards is most frequently used. In this case, selection of the solid standards is important. The solid standards used as calibrants require the following two characteristics: The matrixes of the solid standards should be similar to those of the samples, and the analyte concentrations of the solid standards should be in the range of interest. To accomplish these purposes, certified reference materials (CRMs) are generally used as solid standards. However, this method has a disadvantage, i.e. a blank cannot be easily corrected and quantified. Crucially, no CRMs are available that are suitable for the analysis of silver nanoparticles.

In this study, calibration curves for silicon, phosphorus, and sulphur were constructed using the aforementioned standard solutions containing known amounts of silicate, sulphate, and phosphate, respectively (Fig. 5). To minimize the influence of the differences between the calibrants and samples, the amount of silver in the calibrant should be close to those in the samples, and silver should be vaporized together with analytes in the calibrants when measuring the standard batches. However, a matrix silver solution (i.e. silver nitrate in nitric acid) or nitric acid, which is used as a digestion reagent to prepare silver solutions, that contain only a negligible amount of the analytes, such as silicon, are not available. Therefore, the only silver species that satisfied the requirements was highly purified metallic silver, whose two forms are available: One is a foil or thin plate (99.98%, 0.01 mm thickness) and the other is narrow wire (99.99%, 0.05 mm diameter). In this work, the foil-form silver was adopted because of the ease of preparation of multiple silver plates with the same weight and area using a punch tool. In practice, a 0.8 mm diameter circular plate with a mass of approximately 60 μg was placed in the sample cuvette together with an aliquot of the standard solution of silicon, sulphur, or phosphorus.

To prepare standard batches for the construction of a calibration curve for silver, various volumes of the stock solution of silver(I) were pipetted into empty sample cuvettes, other matrixes and reagents being absent (Fig. 6).

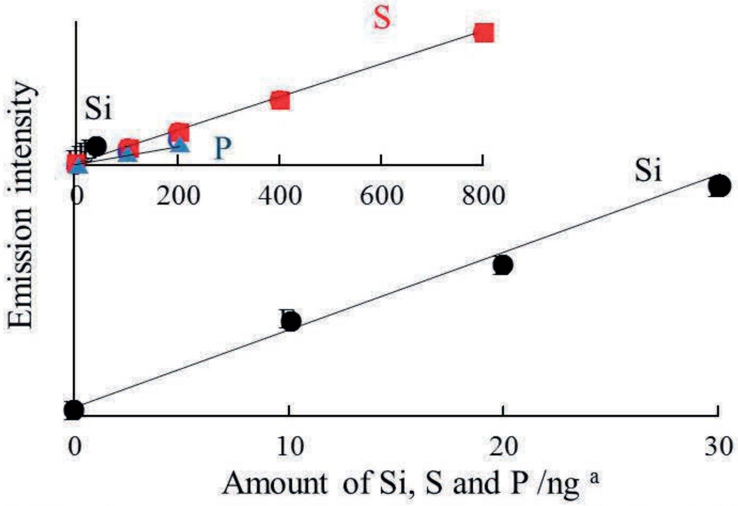

Fig. 5. Calibration curve for the determination of Si, S and P in silver.

a. In the presence of 10 mg Ag.

●, Si; 🟥, S; ▲, P.

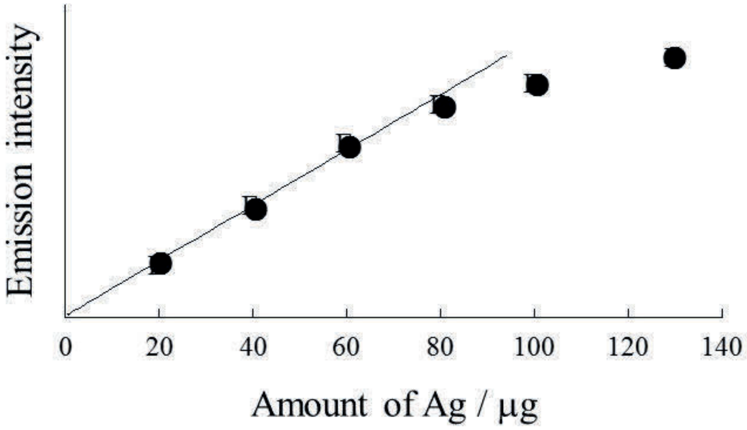

Fig.6. Calibration curve for silver.

2-4-2. Analytical performance

Because realistic blank nanoparticles are not available, the conventional definition of detection limit is inappropriate for direct solid sampling. Therefore, the detection limit was estimated using aqueous standards under the optimum conditions (Table 1). The detection limits for silicon, phosphorus, and sulphur are 1.2, 0.34, and 5.0 ng, respectively. These values were defined as the absolute amounts of the analytes required to yield net peak areas that were three times the standard deviations of the blank in the presence of silver. These values correspond to 15, 4.2, and 62 $\mu g\ g^{-1}$ silicon, phosphorus, and sulphur concentrations in silver nanoparticles (dry powder), respectively. The relative standard deviations were 2.8%, 4.2%, and 2.1% for silicon, phosphorus, and sulphur, respectively; these values were estimated from the results obtained by six replicate measurements of the aqueous standard solutions, each containing 80–100 ng of analyte. The sample cuvette–TBF technique enables the sequential measurement of a number of samples through the preparation of multiple sample cuvettes prior to analysis. Approximately 35 analyses could be carried out per hour. Even with the sampling procedures included, 20 analyses per hour are possible because the tedious weighing procedure with a microbalance is unnecessary.

2-4-3. Application to practical samples in dry form

An attempt was made to examine the application of this method to the determination of silicon, phosphorus, and sulphur in silver nanoparticles. However, neither CRMs for silver nanoparticles nor practical samples in which the contents of the analytes were certified are available. Thus, various silver nanoparticles were prepared from various kinds of highly purified silver. The contents of the analytes were calibrated using a series of measurement data obtained using the following two methods: One is the proposed method by which both the analyte element and matrix silver are estimated by the emission intensities, and the other is the conventional method, in which only the analyte is determined using TBF-ICP-AES and the sample was weighed using a microbalance. As shown in Table 2, the analytical results are in good agreement. Various amounts of silicon, phosphorus, and sulphur were added to the silver nanoparticles. The recovery values were in good agreement with the expected values. To further evaluate the accuracy of the proposed method, the silicon contents were determined semi-quantitatively using an electron probe microanalyzer (EPMA). In this case, since no calibrants were available, a CRM for the analysis of steel samples was used as assumptive standard. Approximately 5 g of sample was required to form a pellet aliquot. Regarding the validation of phosphorus and sulphur, because of the restricted sample amounts, pellet aliquots could not be constructed for EPMA. Therefore, the analytes were leached from one or two gram aliquots of the silver nanoparticles using dilute nitric acid and then detected via nebuliser ICP-AES. As evidenced in Table 2, satisfactory results were obtained. Compared to the reference methods, the proposed direct determination technique has the advantage of requiring only sub-milligram samples for the preparation of a sample batch. Also, neither reagents nor a tedious procedure are required to prepare sample batches, including sample weighing processes.

Table 2. Analytical results of various silver nanoparticles (dry samples)

	Added / mg g^{-1}	Proposed [a] / mg g^{-1}	Conventional [b] / mg g^{-1}	Reference method / mg g^{-1}
Silicon determination				
Sample A	0	1.70 ± 0.04 [c]	1.74 ± 0.17 [c]	1.65[d]
	0.59	2.28	2.30	-
	0.91	2.50	2.72	-
Sample B	0	0.79 ± 0.02 [c]	0.63 ± 0.10 [c]	0.66[d]
Sample C	0	1.65	1.63	1.43[d]
Phosphorus determination				
Sample A	0	4.6 ± 0.3 [c]	4.0 ± 0.1 [c]	4.3 ± 0.1 [c, e]
	3.6	9.3	6.3	-
	10	15	14	-
Sample C	0	3.7	3.9	4.0 ± 0.1 [c, e]
Sulphur determination				
Sample D	0	16 ± 2 [c]	14 ± 6 [c]	16 ± 0.2 [c, e]
	30	49	44	-
	40	51	53	-
Sample E	0	0.55 ± 0.11 [c]	0.42 ± 0.05 [c]	0.44 ± 0.03 [c, e]

a. Calculated by the equation (1), in which sample amount was estimated spectrometrically.

b. Calculated by the equation (1), in which sample amount was weighed with microbalance.

c. Mean ± standard deviation, n=3.

d. Silicon concentration was measured by electron probe microanalyzer.

e. Phosphorus and sulphur were leached out with nitric acid.

The obtained solution was analyzed by nebulizer ICP-AES.

2-4-4. Analyses of samples in suspended solution form

There are various kinds of suspended solutions containing silver nanoparticles. For laboratory use, the following properties are common: Homogeneous, transparent with a yellowish tint, and practically solution-like colloidal suspensions. For these purposes, very dilute aqueous suspensions are favourable (typical concentration of ~0.005%). Therefore, they can be analysed using the same analytical method as that for solution analysis, which includes nebuliser ICP-AES, nebuliser ICP-MS, and ETV-ICP-AES. For industrial materials, however, very viscous suspensions with similar viscosities as honey are often utilised as pastes and gel-inks to manufacture transparent electrodes, membrane wiring boards, and flexible printed circuits. In other words, highly concentrated suspensions are required to convey a useable electroconductivity to the final products. Hence, dense suspensions are essential. To disperse the particles, an organic solvent, such as toluene or 2-butanone, is used depending on the industrial process, polarity of the particles, density of the suspensions, surfactant used, purpose of the final products, and, especially, impurities on the surfaces of the particles. For suspensions with high viscosities, sample uptake by a nebuliser is impossible. It is also difficult to use a pipetting procedure to prepare aliquots with constant volumes because a considerable portion of the sample will remain inside the tip of a digital pipette. However, weighing using a microbalance is also impossible because of the high volatility of the organic solvent.

Determination of sulphur

Four kinds of silver nanoparticles were analysed to evaluate the applicability of the proposed method. The analytical results are listed in Table 3. The results were not acceptable, as there were large discrepancies between the results of conventional weighing and our proposed spectrometric estimation. These discrepancies are likely the result of the species and location of sulphur. That is, a sulphur impurity was likely located around or inside the silver nanoparticles and did not dissolve in the toluene solvent. Despite the presence of a significant excess of surfactant as a dispersing agent and also pipetting under ultrasonication, remarkable segregation was observed in all sample aliquots. To evaluate the segregation, I measured the sedimentation rates of the samples analysed, and the results, which are exhibited as the transparency (%,) are given in Fig.7. Rapid separation and sedimentation occurred in the case of at least three samples. Moreover, as evident from the photo in Fig. 8, the last sample exhibited slow separation after two hours from ultrasonication had stopped. My opinion is that even if a constant volume of a certain toluene suspension was added to a cuvette using the pipetting procedure, less silver was contained in the aliquot. As a result, the conventional calculations, which involve dividing the impurity amounts by the apparent silver weights converted from their liquid volumes, gave lower values than the proposed ones, which involved dividing the impurity amounts by the actual silver amounts. Of course, industrially, the latter is preferable for factory process control.

Table 3. Analytical results of sulphur in various silver nanoparticles (suspension in toluene)

	Sulphur concentration / mg g^{-1}			
Practical sample [a]	Added [b]	Proposed method [b]	Added [c]	Conventional [c]
Sample F [d]	0	0.57 ± 0.04	0	0.21 ± 0.01
	0.33	0.88 ± 0.07	0.12	0.31 ± 0.04
	0.62	1.35 ± 0.02	0.23	0.51 ± 0.02
Sample G [d]	0	1.6 ± 0.1	0	0.4 ± 0.1
	0.3	1.8 ± 0.2	0.1	0.4 ± 0.1
	0.9	2.9 ± 0.1	0.2	0.6 ± 0.1
	1.8	4.0 ± 0.1	0.4	1.0 ± 0.1
Sample H [e]	0	2.9 ± 0.3	0	0.69 ± 0.13
	4.0	7.2 ± 0.6	1.1	1.9 ± 0.1
	9.1	12 [f]	1.6	2.1 [f]
Sample I [e]	0	0	0	0
	1.3	1.2 ± 0.1	1.1	0.70 ± 0.65
	2.0	1.8 ± 0.1	1.1	0.94 ± 0.04

a. Sample F and G were purchased, while sample H and I were home-made silver nanoparticles.

b. Calculated by the equation (1), in which sample amount was estimated spectrometrically.

c. Calculated by the equation (1), in which sample amount was assessed by the prepared amount of sample in suspension. By the sedimentation, therefore, overestimation of the sample amount taken is considered in each batch.

d. Mean ± standard deviation, n = 3.

e. Mean ± differences from mean value, n = 2.

f. A single datum.

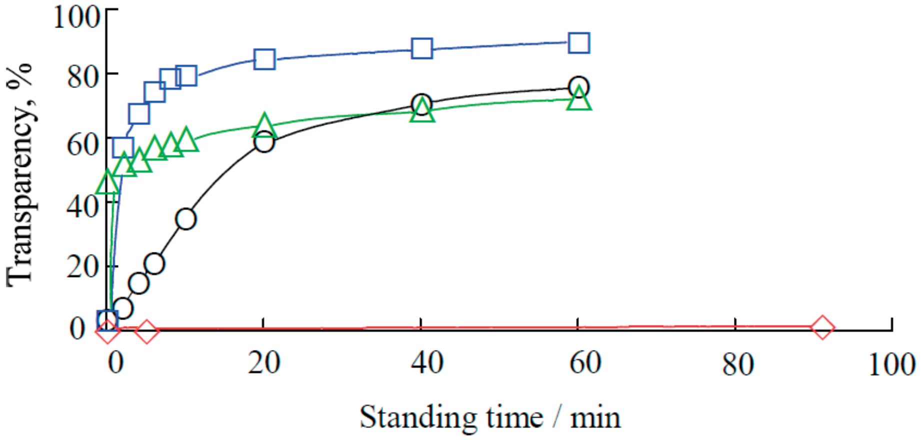

Fig. 7. Effect of transparency on the standing time of silver nanoparticles.

□ , Sample F; ○, Sample G; △, Sample H, and ◇, Sample I.

With increasing the standing time, transparency decreased rapidly, except the sample I. This means that the silver nanoparticles were sedimented, the top layer being cleared.

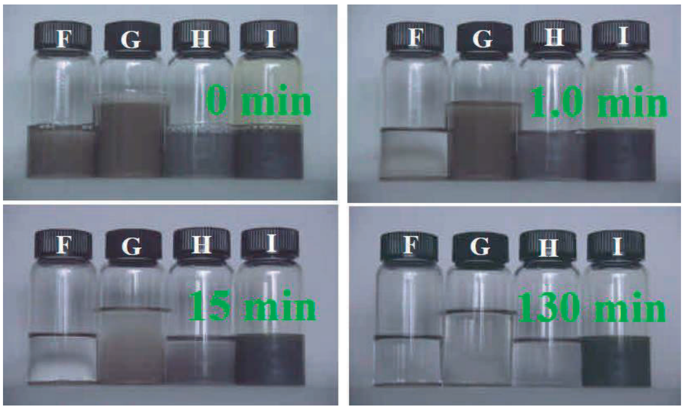

Fig. 8. Photographs of silver nanoparticles.

Samples F, G, H, and I are the same sample in Table 3. Concentration of silver nanoparticles, approximately 0.1%; Triton X-100 as surfactant, ca. 10%; solvent, toluene.

0 min (just after mixing with ultrasonic generator), there are various bubbles at the surface between toluene and air; 1 min, upper phase of sample F becomes clear; 15 min, upper phases of sample G and H becomes clear in some extent; 130 min, the surface between toluene and air of sample I is slightly transparent, while the silver nanoparticles of sample F, G, and H are precipitated completely.

Determination of phosphorus

To establish the applicability of the method for phosphorus determination, several toluene suspension of silver nanoparticles were analysed. The quantification was carried out using the external calibration curve method with the aqueous standard solution of phosphate ions in the presence of silver(I) ions. The results are summarised in Table 4, which shows that satisfactory results and recoveries were obtained. Contrary to the results regarding the determination of sulphur, both the data from the proposed ETV method and conventional calculations were in good agreement. This means that phosphorus is homogenously distributed.

Table 4. Analytical results of phosphorus in various silver nanoparticles (suspension in toluene)

	Phosphorus concentration / mg g^{-1}			
Practical sample	Added [a]	Proposed method [a]	Added [b]	Conventional [b]
Sample J [c]	0	1.1±0.1	0	1.1±0.1
	0.8	1.9±0.1	0.8	2.0±0.1
	1.3	2.5±0.1	1.2	2.4±0.1
	2.1	3.5±0.3	2.0	3.3±0.2
	4.4	5.8 [d]	4.0	5.3 [d]
Sample K [e]	0	5.1±0.1	0	5.3±0.1
	1.1	6.3±0.6	1.3	7.2±0.5
	2.7	6.9±0.1	2.6	6.7±0.2
	4.5	8.9±0.1	5.2	10.2±0.1
Sample L [e]	0	0	0	0.27
	4.9	4.6±0.1	5.2	5.3±0.1
	19	18±1	20	19±1
Sample M [e]	0	2.4±0.2	0	2.1±0.1
	11	13±1	11	13±1
	24	24±1	21	22±1
	47	46±2	43	41±1

a. Calculated by the equation (1), in which sample amount was estimated spectrometrically.

b. Calculated by the equation (1), in which sample amount was assessed by the prepared amount of sample in suspension. By the sedimentation, therefore, overestimation of the sample amount taken is considered in each batch.

c. Mean ± standard deviation, n = 4.

d. A single datum.

e. Mean ± differences from mean value, n = 2.

2-5. Conclusion

An analytical procedure for the direct analysis of silver nanoparticles by ETV-ICP-AES was proposed. An exchangeable small sample cuvette made of tungsten was utilised as a direct solid sampler and vaporiser via incorporation of a tungsten boat furnace vaporiser. The method was successfully applied to the determination of silicon, phosphorus, and sulphur in silver nanoparticles and also permits facile standardisation by using aqueous standard solutions. The sample amount in each aliquot was estimated spectrometrically, which eliminated the need for tedious and time-consuming sample weighing procedures along with any pretreatment and/or predigestion. This method is suitable for not only the screening but also accurate analysis of silver nanoparticles for industrial use, regardless of whether they are in a liquid suspension or dry particle form.

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Chapter 3

Direct solid sampling system for electrothermal vaporization and its application to the determination of chlorine in nanopowder samples by inductively coupled plasma atomic emission spectrometry

3-1. Summary

An electrothermal vaporization (ETV) system using a tungsten boat furnace (TBF) sample cuvette was designed for the direct determination of chlorine in metallic nanoparticles and fine powder samples with detection by inductively coupled plasma atomic emission spectrometry (ICP-AES). A portion of a powder or particle sample was placed into a small tungsten sample cuvette and weighed accurately. A modifier solution of aqueous or alcoholic potassium hydroxide was added to it. Then, the cuvette was positioned on the TBF incorporated into the ETV apparatus. The analyte was vaporized and introduced into the ICP atomic emission spectrometer with a carrier gas stream of argon and hydrogen. The metal samples were analyzed by using an external calibration curve prepared from aqueous standard solutions. Few chemical species including analyte and some chlorine-free species were introduced into the ICP, because the analyte has been separated from the matrix before introduction. Under such dry plasma conditions, the energy of plasma discharge was focused on the excitation of chlorine atoms, and as a result, lower detection limits were achieved. A detection limit of 170 ng g^{-1} of chlorine in solid metal samples was established when 60 mg sample was used. The relative standard deviation for 16 replicate measurements obtained with 100 ng chlorine was 8.7%. Approximately 30 batches could be vaporized per hour. The analytical results for various nanoparticles (iron (III) oxide, copper, and silver) and metallic fine powder samples (silver and gold) are described.

3-2. Introduction

Halogenated compounds containing chlorine and bromine have been used as flame-retardants for electrical products, automobiles, building materials, and so on. Recently, national governments and economic organizations began enforcing restrictions for halogens due to environmental conservation concerns [1]. Furthermore, halogens can deteriorate product properties. These effects considerably increase with a decrease in the size of materials. For instance, metallic nanoparticles have been applied as inks and pastes in the flexible electronic circuitry industry, as fluorescence enhancers in the areas of fluorophore-medical biosensing or bioimaging, as heterogeneous catalysts for chemical syntheses or degradation processes, and as optical devices. Therefore, efforts have been made to reduce the halogen content in these products. When producing high quality nanoparticles, it is important to determine and control minor elements, such as chlorine, during the manufacturing process. Even very low concentrations of chlorine can cause observable negative effects. Sensitive analytical methods are required to determine chlorine content in such particle samples. Various techniques have been applied for the determination of chlorine, which depend on the analyte concentration and the sample matrix analyzed. X-ray fluorescence spectrometry (XRF) [2, 3], neutron activation analysis [4] and direct solid sampling ETV atomic spectrometry [5, 6] have been used for the direct analysis of solid samples. Ion-selective electrodes [7], ion chromatography (IC) with a conductivity detector [8-10], chemiluminescence [11], capillary electrophoresis with a UV detector [12], gas chromatography-mass spectrometry (GC-MS) [13], high-resolution continuum source molecular absorption spectrometry [14, 15], nebulizer ICP-MS [16], and nebulizer ICP-AES are generally used for the determination of trace chlorine in aqueous samples [17]. These methods require pretreatment for digestion, dissolution, separation, and sometimes derivatization, to convert solid samples into liquid or gaseous forms. The use of oxidative mineral acids (e.g., nitric acid) is essential in the conventional wet digestion of silver and copper. However, the analyte is lost during these pretreatment procedures because of the high volatility of chlorine species. This problem can be overcome by performing digestion in high-pressure bombs or closed digestion vessels [7]. However, if aqua regia is used for digestion (e.g., for metallic gold), hydrochloric acid leads to severe contamination of the sample by chloride ions. In general, pneumatic nebulizer ICP-MS exhibits the lowest detection limits for the determination of metallic elements in a variety of matrixes. However, because nebulization only allows a small portion of the solution mist to actually reach the ICP, almost all the solution is wasted. In ICP-MS, the $^{35}Cl^+$ ion is overlapped by $^{18}O^{16}O^1H^+$ molecular ion while the $^{37}Cl^+$ ion is interfered with by the $^{36}Ar^1H^+$ ion. These major spectral interferences can be isolated by using a high-resolution (HR)-ICP mass spectrometer [18]. Even if either an HR-ICP or a quadrupole ICP instrument was used, the obtained detection limit will be poorer than expected. Another issue is that the ionization source of an argon ICP does not provide sufficient energy to ionize a chlorine atom. The degree of ionization was estimated to be only 0.9 % when an aqueous sample solution was introduced into an ICP discharge via nebulizer. [19] The sensitivity is further decreased by the introduction of water mist, which accompanies the nebulization of the aqueous sample solution. Despite the poor situations, the detection limits obtained by a solution nebulization was reported to be 730 ng mL^{-1} and 3 ng mL^{-1} with quadrupole [20] and high-resolution [18] ICP mass spectrometers. Theoretically, excitation requires less energy than ionization of the same atomic species. ICP-AES is probably a more favorable technique for the determination of chlorine because of its robustness, simplicity, high accuracy, and because the atomic emission line of chlorine is free from spectral interference. In either of the ICP atomic spectroscopic techniques, the digestion and/or dissolution problem remains when a nebulizer is used as a sample introduction device. Consequently, I think the pretreatment step is critical to the determination of chlorine in metal samples by either of the ICP atomic spectrometry techniques.

Direct solid sampling is a technique where solid samples are introduced directly into the ICP spectrometer with no pretreatment procedure. The technique provides the following advantages over conventional nebulization: increased transport efficiency, small sample size, no dilution due to sample dissolution, and no contamination due to sample preparation. Furthermore, using an ETV technique combined with ICP atomic spectrometry allows for the selective vaporization of the analyte. That is, in this method, volatile solvents are expelled before, and the nonvolatile matrix is retained in the furnace during the selective introduction of the analyte into the plasma. This results in effective excitation of atomic chlorine and leads to the sensitive determination of chlorine species in solid sample materials. Hashimoto et al. focused on the significant difference between vaporization properties of the analyte and the matrix, and demonstrated the use of a small sample cuvette-tungsten boat furnace system for the direct determination of chlorine in fine ceramic materials by ICP-AES [21]. That is, the surface of the solid ceramic sample was leached by using potassium hydroxide solution in the sample cuvette. The cuvette was then positioned on a tungsten boat furnace incorporated into an ETV apparatus, and chlorine was selectively vaporized and introduced into the plasma. This analysis was restricted to the surface of ceramic materials [21]; here it was established the direct determination of trace chlorine species in samples of various metallic nano- / fine particles.

3-3. Experimental

3-3-1. Apparatus and reagents

A series of tungsten sample cuvettes (10 mm x 20 mm; with a bottom depression of 6 mm x 6 mm) were used as sampling dishes, sample carriers, and vaporizers in an electrothermal vaporization. A tungsten boat furnace (10 mm x 60 mm; with a bottom depression the size of the sample cuvettes) was purchased from SII NanoTechnology (Tokyo, Japan). An atomic emission spectrometer (Horiba Jobin Yvon Model Ultima2 ICP, Longjumeau, Cedex, France) and an electrothermal atomizer unit (Rakuyo Giken Model RH-21, Kumiyama-Town, Kyoto, Japan) were used for the TBF-ICP-AES. Their setup was described previously [21]. A semi-microbalance (A&D Co. Model GR-120, Tokyo, Japan), whose readability was 0.01 mg, was used to weigh the powdered sample in the cuvette. A pair of titanium tweezers (As-One, Osaka, Japan) and Teflon watch glasses (As-One) were used for handling the sample cuvettes. A hotplate (Maruto Model MS-160, Tokyo, Japan), whose maximum heating temperature was 180ºC, was used to expel solvents from a series of the sample cuvettes.

A 325-mesh gold particles (99.999%, Nilaco, Tokyo, Japan), 40-nm colloidal gold solution (British Biocell International, Cardiff, UK), 50-nm silver nanoparticles [22], 2-μm fine silver particles (99.9%, Kojyundo Chemical Lab., Sakado, Japan), 200-nm copper nanoparticles [23], and 200-nm iron oxide nanoparticles (99.5%, Toda Kogyo) were prepared or purchased from their respective companies. A fine particles of silicon carbide were purchased as a JCRM series (The Ceramic Society of Japan, Tokyo, Japan) ceramic certified reference material. A traceable standard reagent NAC-st1 (4-chlorobenzenesulphon-2-bromo-4-fluoroaniline) was provided by Nac Techno Service (Tokyo, Japan). An organic standard solution was prepared by dissolving 514.3 mg NAC-st1 in 100 mL of ethanol, resulting in a chlorine concentration of 500.0 mg L^{-1}. A 1000 mg L^{-1} ion-chromatography standard solution of chloride ion was purchased from

Kishida Chemical (Osaka, Japan). Working standards of the organic and inorganic solutions were prepared by diluting appropriate aliquots of the corresponding standard solution with ethanol or water, respectively. As chemical modifiers, an aqueous and an alcoholic solutions of 40 mmol L^{-1} potassium hydroxide were prepared by dissolving 0.48 g of potassium hydroxide monohydrate (Suprapur, Merck, Darmstadt, Germany) in 100 mL of water or ethanol, respectively. A 40-nm colloidal silver solution (British Biocell International, United Kingdom) was used for the construction of a calibration curve as a chlorine-free metal matrix.

3-3-2. Recommended procedure for routine analysis

The sample cuvettes were preconditioned by soaking in dilute nitric acid solution, followed by heating to expel chlorine impurities, and then confirming a blank signal level. Using a microbalance, each aliquot of the samples of micro- or nano-size particles (approximately up to 60 mg) was weighed accurately into a sample cuvette. In the case that samples were in liquid form or colloidal solution, each aliquot was taken with a digital micropipette. To construct a calibration curve, a 20 μL aliquot of the colloid silver solution was placed into an empty sample cuvette. Into it, aqueous standard solution was pipetted. A 20 μL aliquot of either aqueous or ethanolic modifier solution was added depending on the hydrophobicity of the particle surface analyzed. These cuvettes were placed on the hot plate at 110ºC until most of the solvent was evaporated, typically for 3 min.

One of the dried sample cuvettes, on which samples adhered weakly, was positioned on the TBF that was incorporated into the ETV device. The TBF was warmed for 25 s at 70 ºC and then maintained at 200 ºC for 60 s to completely expel any remaining solvent through the open sample insertion port. After the sample had dried and the sample insertion port was closed with a glass stopper, the temperature was raised to 1800 ºC over 6 s followed by a hold time of 3 s for the vaporization of the analyte species. The vapor, which was presumed to be potassium chloride, was introduced into the ICP through a perfluoroalkoxy (PFA) tube by the carrier gas at a flow rate of 800 mL min^{-1} (H_2, 7%; Ar, 93%). A transient signal at 134.724 nm was recorded as an atomic emission of chlorine. The peak profile was recorded with a personal computer (IBM PC/AT compatible) attached to the spectrometer. The peak height was used for the evaluation, although the peak area was measurable simultaneously. The recommended operating conditions are summarized in Table 5.

Table 5. Instrument operation conditions for determination of chlorine

ICP atomic emission spectrometer (Horiba Jobin Yvon S.A.S. Model Ultima2)	
R.F. incident power	1.3 kW
Argon gas flow rate	
Plasma argon gas	15 L min^{-1}
Auxiliary argon gas	0 L min^{-1}
Analytical line	Cl I 134.724 nm
Observation height	7 mm above load coil
Tungsten boat furnace vaporizer (Rakuyo Giken Model RH-21)	
Sample amount	~ 60 mg
Chemical modifier	40 mmol L^{-1} KOH 20 μL
Drying	70ºC for 25 s
Ashing	200ºC for 60 s
Vaporization	1800ºC for 3 s (ramp 6 s)
Carrier argon gas	744 mL min^{-1}
Carrier hydrogen gas	56 mL min^{-1}

3-4. Results and Discussion

3-4-1. Optimization for the direct solid sampling ETV procedure

An advantage of the ETV procedure for the analysis of liquid samples is that the same amount of a sample solution can be pipetted repeatedly into the furnace incorporated in the vaporizer device. However, for the direct analysis of solid samples, the same amount of solid sample aliquot cannot be taken repeatedly. Therefore, a method for accurately pre-weighing small amounts of powdered samples and introducing them conveniently into the device, and for removing the remaining residues completely, was needed. Graphite furnace AAS, incorporating an automated solid sampling accessory and a microbalance system, showed promising features [24]. This technique has been applied to the analysis of graphite [25], charcoal [26], carbon nano-tube materials [24, 27], and tantalum micro-particles [28]. Lüdke et al. reported a solid sampling ETV-ICP-MS for the analysis of particulate matter in air, in which graphite tubes and cups were used [29]. Higher temperatures can be achieved more rapidly by using metal furnaces when compared to graphite furnaces. Okamoto et al. demonstrated a magnetic drop-in tungsten boat furnace (TBF) vaporization ICP-AES for the determination of trace elements (S, Se, Sb, Bi) in iron and steel samples [30, 31]. This earlier approach used a long needle-shaped magnet, exchangeable sample cuvettes, and a TBF vaporizer system. A steel sample was held over a TBF with the needle magnet. When the temperature of the sample was raised to its Curie point, it dropped into the TBF and melted to generate analyte vapor. The magnetic drop-in procedure is doubtlessly useful for the analysis of magnetic samples, but it is not applicable for non-ferrous metal samples. In this experiment, each aliquot of the metal powder samples was weighed directly into a cuvette. The sample cuvettes were used as weighing dishes, sample carriers, and electrothermal vaporizers. Each cuvette can be positioned closely to the TBF, because all of the sample cuvettes and TBFs were formed from tungsten plates by pressing in an identical metallic mold. This resulted in the repeatable thermal conduction from the TBF to the sample cuvette, and consequently, reproducible signals were obtained.

To optimize the ETV operating conditions, the ICP signals were recorded from aliquots of approximately 10 mg of the 50-nm silver nanopowder as a typical sample. Under the direct solid sampling TBF system without any modifier, a very tiny signal assignable to chlorine atomic emission was observed. The analyte vaporized and caused a significant loss before its introduction to the plasma because the chloride ion and other chlorine species are volatile compared to most of the metallic elements. Therefore, it was necessary to add some chemical modifier(s) to retain the analyte until the desired vaporization and introduction stage. Tetramethylammonium hydroxide (TMAH) has been used as a suitable modifier for the determination of halogens in aqueous samples by TBF-ICP atomic spectrometry [32] [33]. In the presence of TMAH, the analyte was expected to convert into the chloride salt of the TMA^+ ion. However, it is necessary to maintain a higher ashing temperature when performing the direct analysis of solid samples by ETV. If TMAH was applied, the modifier would decompose to trimethylamine and methanol at the distillation temperature because the salt, TMACl, is not thermally stable. Additionally, the TMAH would be removed completely at approximately 200°C. Instead, in this experiment, potassium hydroxide solution was used as a chemical modifier. As Fig. 9 shows, the sensitivity was constant, but slightly decreased, over the range of 0.5–1.0 μmol of added potassium hydroxide. 0.8 μmol was selected as a suitable amount of potassium hydroxide. Nano- or micro- particles exhibit either hydrophilicity or hydrophobicity depending on the method of their preparation, additives, and their suspension medium if they are in liquid form. The modifier was prepared as aqueous or ethanolic solution depending on the affinity of the samples for water. Since almost all the samples used exhibit hydrophobicity, potassium hydroxide was prepared as a solution in ethanol. For the analysis of gold samples and silver nanoparticles, which were hydrophilic, therefore an aqueous potassium hydroxide solution was used.

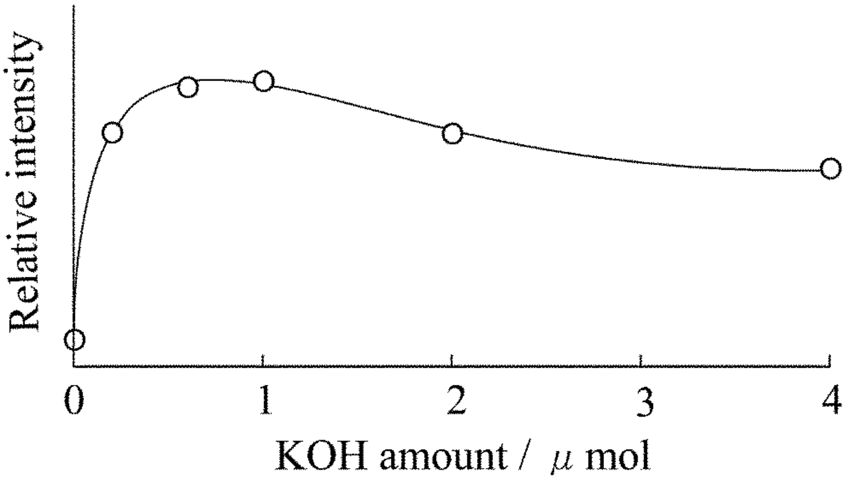

Fig. 9. Effect of KOH amount on the emission intensity of chlorine.

Sample, approximately 10 mg of 50 nm silver nanopowder. Instrument operating conditions are as in Table 5.

A 200 ºC ashing temperature was suitable to expel the solvent of modifier. When the vaporization temperature was lower than 1500 ºC, somewhat poor sensitivities were obtained. As Fig 10 shows, maximum and constant peak height was achieved in the temperature range of 1800 – 2600 ºC. Therefore, 1800 ºC was settled as the optimum vaporization temperature.

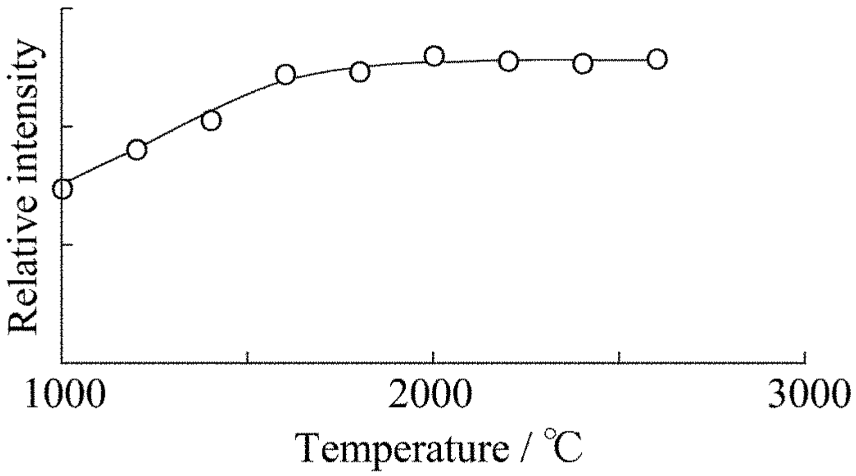

Fig. 10. Effect of vaporization temperature on the atomic emission intensity of chlorine.

Sample, approximately 10 mg of 50 nm silver nanopowder. Instrument operating conditions are as in Table 5.

3-4-2. Evaluation of standards

It was necessary for the construction of the calibration curve that the standards have a similar matrix to those of the sample. Here, a colloidal silver solution was used as a chlorine-free metal particle sample, because no signal assignable to atomic emission of chlorine was observed when it was analyzed. To establish the external calibration curve, a 20 μL aliquot of the colloidal silver solution was placed in each sample cuvette prior to the injection of a known amount of the aqueous standard solution.

Fine inorganic particles can contain several chlorine-containing species such as the chloride ion, the chlorate ion, and organochlorine species. If the particle samples contain more than one chlorine compound, and if each chlorine species exhibits different sensitivities, the chlorine calibration curves for the corresponding compounds should be constructed to determine each of the analyte species present. To evaluate the inorganic chlorine species, the atomic emission intensities were measured using aqueous solutions containing the chloride ion, the chlorate ion, or the perchlorate ion. To supply calibrants to be used in a hydrophobic medium, NAC-st1 solution in ethanol was investigated as an organic standard, because traceability of the NAC-st1 has been established and the compound has a large gravimetric factor. As Fig. 11 shows, the sensitivities obtained did not depend on the chemical species of chlorine or their media. Therefore, a 1000 mg L^{-1} ion chromatography standard solution of chloride ion and a 500 mg L^{-1} NAC-st1 in solution in ethanol were used as standard stock solutions.

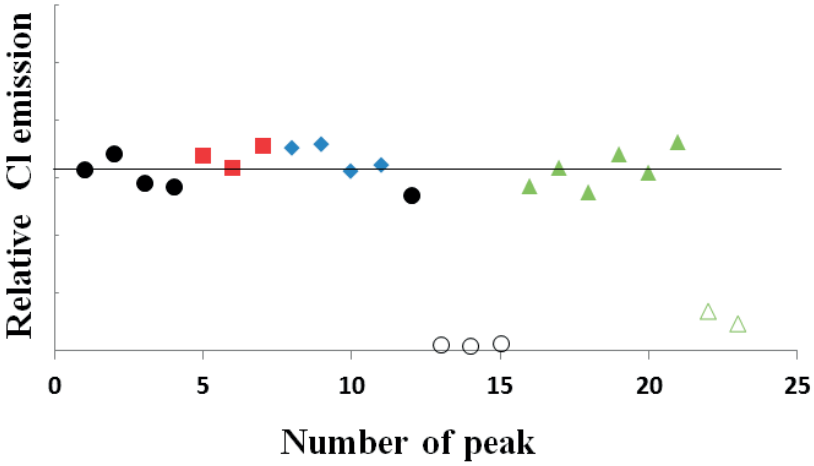

Fig. 11. Sensitivity comparison of chlorine species

●, Chloride ion; ■, chlorate ion; ◆, perchlorate ion;

▲, NAC-st1. ○, blank; △, NAC-st2.

3-4-3. Interference study

The effects of foreign cations and anions on the vaporization of chlorine were investigated according to the recommended procedure. The tolerance limit of foreign ions, which was the amount that gave less than ±10% error for the measurement of chlorine, was determined. The results are presented in Table 6. Since the vaporization temperature was relatively low compared to that of the conventional ETV technique, few metal ions were vaporized and introduced into the ICP. The reduced interference was also due to the strongly basic potassium hydroxide medium. That is, the metal ions formed into their hydroxide salts, which were generally nonvolatile. While chloride species were converted potassium chloride, which was suitable species for the vaporization in the ETV procedure.

Table 6. Tolerance limits of foreign ions for determination of chlorine (results within 10% error)

Ion	Mass ratio (foreign ion / chlorine[a])	Ion	Mass ratio (foreign ion / chlorine[a])
Na^+	>230	Ni^{2+}	>500
Mg^{2+}	>700	Cu^{2+}	1000
Ca^{2+}	2000	Zn^{2+}	1000
Mn^{2+}	550	Pb^{2+}	>750
Fe^{3+}	>380	I^-	>1790
Co^{2+}	1000	Br^-	800

a) Cl^-, 100 ng. With KOH, 22.4 μg

3-4-4. Application to real samples

Attempts were made to evaluate the application of this method to the determination of chlorine in nano- or micro-metal particles. However, there were no certified reference materials of metal particles for chlorine determination. An available silicon carbide certified reference material was examined instead of metal particles. Various real samples were commercially purchased and investigated. To evaluate the accuracy of the proposed method, various amounts of chlorine were added to each sample. These samples were directly analyzed as received, with no pretreatment. An external calibration curve was constructed using the aqueous potassium hydroxide solution as a modifier, the chloride standard solution in sodium salt form, and the colloidal silver solution as a matrix. Potassium hydroxide and the NAC-st1 solutions in ethanol, if necessary, were added as a modifier and spike solution, respectively, except for with silver nanoparticles, gold samples, and silicon carbide, wherein aqueous modifier and spike solutions were added because of the hydrophilicity of the samples. The results are listed in Table 7, which shows that satisfactory results and recoveries were obtained by the external calibration curve method using the aqueous standard solution of chloride ion.

Table 7. Analytical results of chlorine in metallic nanoparticles and fine metal powder samples

Sample	Added / μg g^{-1}	Found / μg g^{-1}	Expected/ μg g^{-1}
Ag nanopowder	0	50±4	-
(Homemade, 50 nm)	38	93	88
	41	91±4	91
	42	98	92
	79	121	129
	120	160	170
Ag fine powder	0	290±50	-
(2 μm)	90	360	380
	180	440	470
	200	490	490
	320	640	610
Au nanopowder	0	28±1	-
(40 nm colloid soln.)	10	38±1	38
	20	47±1	48
Au fine powder	0	150±3	-
(325 mesh)			
Cu nanopowder	0	54±5	-
(Homemade, 200 nm)	25	81	79
	41	97	95
	44	100	98

Fe_2O_3 nanopowder (200 nm)	0	370±10	-
	333	700±120	703
SiC fine powder (JCRM R021)	0	53±3	(68±14)[a]

[a] Certified value.

3-4-5. Basic analytical performance characteristics

The detection limit of the absolute amount of chlorine was estimated to be 10.4 ng, which was defined as the absolute amount of chlorine required to yield a net peak height that was three times the standard deviation of the sample batches, each containing several-milligram aliquots of the silver nanopowder, in the presence of the potassium hydroxide modifier. This value corresponds to 0.17 μg g^{-1} of chlorine in solid samples, when 60 mg of a sample aliquot was placed on the sample cuvette. Regarding the method detection limit in solid materials, a proportionally lower detection limit could be attained with a large sample amount. As Fig. 12 shows, less than 60 mg of the sample powder can be placed into the cuvette. Table 8 summarized the detection limits of various methods together with our results. In comparison with other detection techniques, superior method detection limit have been achieved by the proposed ETV-ICP-AES.

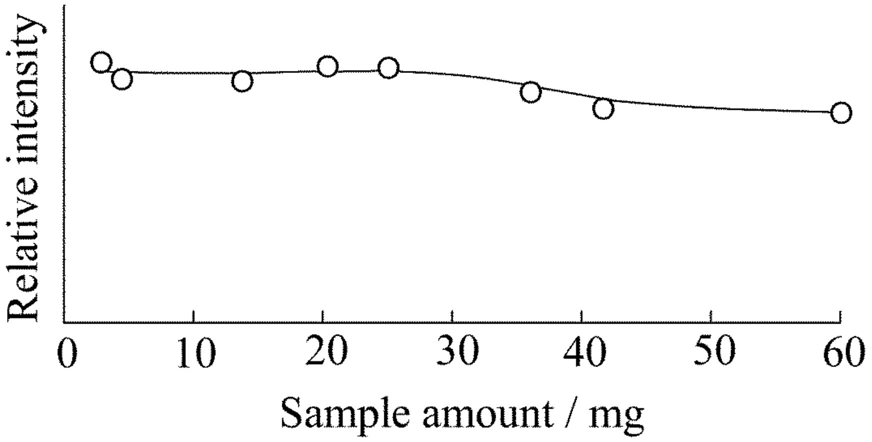

Fig. 12. Effect of sample amount on the atomic emission intensity of chlorine.

Sample, 50 nm silver nanopowder. Instrument operating conditions are as in Table 5.

Table 8. Detection limits of chlorine by various analytical methods

Analytical method	Detection limit of chlorine		
	ng g^{-1} [a]	μg L^{-1} [b]	Ref.
For the analysis of solid samples			
Proposed ETV-ICP-AES	170	(10.4 ng)[c]	-
Our previous ETV-ICP-AES [d]	59[e]	(0.71 ng)[c]	21
Nebulizer ICP-AES following microwave-induced combustion	6000	-	17
Direct solid sampling ETV-ICP-MS	7000		5
ETV-ICP-MS	1050	-	34
Nebulizer DRC ICP-MS	1200	-	16
Direct solid sampling high-resolution continuum source graphite furnace molecular absorption spectrometry	(2000)[f]	(1.0ng)[c]	6
High-resolution continuum source graphite furnace molecular absorption spectrometry	9000	(1.2 ng)[c]	14
Energy dispersive X-ray fluorescence spectrometry	8600	-	2
Isotope dilution thermal ionization mass spectrometry	-	(300 ng)[c]	35
Ion-selective electrode following microwave-assisted digestion	1900	-	7
Ion chromatography following oxygen combustion	2000	10	9
Ion chromatography following oxygen bomb combustion	8000	2	8

For the analysis of liquid samples			
Nebulizer ICP-MS	-	1500	36
Nebulizer high resolution ICP-MS	-	3.25	18
GC-MS following electrophilic addition to styrene[g]	-	100	13
High-resolution continuum source flame molecular absorption spectrometry	-	3000	15
Capillary zone electrophoresis	-	20000	12
Poly(luminol) based chemiluminescence sensor array[g]	-	17.75	11

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[a] Concentration of chlorine in solid sample.

[b] Concentration of chlorine in liquid samples or liquidized samples by digestion.

[c] Absolute amount of chlorine.

[d] Under the conditions optimized for the analysis of ceramic samples

[e] For the analysis of silicon carbide and silicon nitride.

[f] Detection limit is not present. The value was estimated from the sample amount taken (0.5 mg) and the absolute amount of detection limit (1.0 ng).

[g] For the determination of hypochlorous acid or hydrochlorite ion only.

A linear calibration graph for chlorine content covering absolute amounts of up to at least 1600 ng and intersecting the origin of the coordinate axes was established. The relative standard deviation was 8.7%, which was estimated from the results obtained by 16 replicate firings of the sample cuvettes, each containing 100 ng chloride ion added as an aqueous solution of sodium chloride and several milligrams of silver nano-metal powder sample. The proposed sample cuvette TBF system makes it possible to analyze many samples sequentially by preparing many sample cuvettes ahead of time. The throughput was approximately 30 samples per hour.

3-5. Conclusion

Tungsten boat furnace vaporizer and an exchangeable sample cuvette system were used as a direct solid sampler, followed by detection with an ICP atomic emission spectrometry. A series of small sample cuvettes was used as weighing dishes, sample carriers, and electrothermal vaporizers. This technique simplified parts of the analytical process such as weighing of small amounts of powdered or particle samples, decomposition of solid materials, introduction of the samples into the vaporization device, and removal of the residues from it. The technique permitted an easier standardization procedure by using aqueous standard solutions. Because of the quite easy procedure, so-called "with no skill" operation, this methodology is useful for the screening and accurate analysis of nanopowders and metallic fine powder samples.

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General Conclusion

An analytical procedure for the direct analysis of fine particles by ETV-ICP-AES was proposed. An exchangeable small sample cuvette made of tungsten was utilised as a direct solid sampler and vaporiser via incorporation of a tungsten boat furnace vaporiser. The methods were successfully applied to the determination of impurities such as silicon, phosphorus, sulphur and chlorine in fine particles. Rapid and accurate determination for fine particles without any pretreatment and/or predigestion were achieved. There are possibilities of applications not only for elements in fine particles studied in this research but also other impurities. This methodology is effective industrially. Furthermore, this is suitable for the analysis of nanoparticles because the handling time for nanoparticles which presents a danger to public health are reduced.

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公表論文

(1) Spectrometric estimation of sample amount in aliquot for a direct solid sampling system and its application to the determination of trace impurities in silver nanoparticles by ETV-ICP-OES.

Kenichi Nakata, Yasuaki Okamoto, Syoji Ishizaka, and Terufumi Fujiwara, *Talanta*, **150**, 434-439 (2016).

(2) Direct solid sampling system for electrothermal vaporization and its application to the determination of chlorine in nanopowder samples by inductively coupled plasma optical emission spectroscopy.

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参考論文

(1) Determination of thallium by heated quartz cell atomic absorption spectrometry with tungsten boat furnace vaporizer, Yasuaki Okamoto, Kenichi Nakata, Terufumi Fujiwara, and Takahiro Kumamaru, *Analytical Sciences*, **13**, 299-301 (1997).

Notes

Determination of Thallium by Heated Quartz Cell Atomic Absorption Spectrometry with Tungsten Boat Furnace Vaporizer

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Keywords Thallium, electrothermal vaporization, tungsten boat furnace, heated quartz cell atomic absorption spectrometry

Sample introduction by electrothermal vaporization (ETV) is well known as one of the most useful techniques for inductively coupled plasma atomic emission spectrometry (ICP-AES). There have been numerous applications of the technique since the first publication in 1974 describing the use of a tantalum filament vaporizer.[1] Various metals and graphite have been used as furnace construction materials, depending on the elements to be determined and the matrix to be analyzed. However, the introduction technique has not be combined with atomic absorption spectrometry (AAS).

In our previous papers, we described a tungsten boat furnace (TBF) atomizer originally manufactured for AAS which was modified for the ETV-heated quartz cell (HQC)-AA spectrometric determination of lead[2] and cobalt.[3] By using the system, inorganic lead(II) or cobalt(II) was converted to organic lead or cobalt species by applying Grignard reagents. Since the analytes were converted from inorganic matrices to introduce them into the atomic spectrometer, essentially no interference from most inorganic ions was observed.[2] Therefore, these proposed methods could be applied to the determination of metals even in complex matrices.

Regarding the low boiling metal elements, the analyte can be easily vaporized without *in situ* chemical modification as done above and still be effectively introduced into the atomic spectrometer even with relatively mild thermal conditions. We have observed that thallium, thermally vaporized from a TBF, absorbed the atomic radiation from a thallium hollow cathode lamp while passing through a quartz cell heated to over 700°C. In this research, TBF vaporization and introduction to an HQC for the detection of thallium by AAS was demonstrated. This method was applied to the analyses of some raticides. HQC is one of the most effective accessories for AAS to improve sensitivities because of its long optical path. However, the temperature (approximately 1000°C) is too low to atomize those elements except for the limited chemical species such as organometal compounds and volatile hydrides, *etc.* For thallium, there has been no previous paper dealing with its ETV-HQC-AA spectrometric determination, although the conventional electrothermal atomic absorption spectrometric methods have been reported.[4-7]

Experimental

Apparatus

A Nippon Jarrell-Ash (Uji; Model AA-8200) two-channel atomic absorption spectrometer equipped with a Nippon Jarrell-Ash (Model HYD-20) HQC atomizer, a Hamamatsu Photonics (Toyooka; Model L233-81NU) thallium hollow cathode lamp and a (Model L544-20) deuterium arc lamp was used. For electrothermal sample introduction, a Seiko II (Chiba; Model SAS-705V) metal furnace atomizer for AAS equipped with a tungsten boat (large U-type, 10 mm×60 mm) was used after some modifications. A diagram of the vaporization device was shown in the literature.[2] Both background-corrected atomic absorption signal and background signal were recorded with a Rikadenki (Tokyo; Model B-381) three-channel strip chart recorder. An integrated background-corrected atomic absorption signal was estimated with a Shimadzu (Kyoto; Model Chromatopac C-R1A) integrator.

Reagents

All chemicals were of analytical-reagent grade. A thallium(I) stock standard solution for AAS (1000 mg dm^{-3}; Kanto Chemical, Tokyo) was diluted with 0.1 mol dm^{-3} nitric acid as required.

Recommended procedure

The recommended procedure for the operation of the TBF device was as follows: 100 mm^3 of an aqueous sample solution containing not more than 80 ng of thallium was pipetted into the tungsten boat. The boat was then heated for 210 s at 120°C to remove the solvent and the injection hatch was closed by a silicone rubber stopper. To pyrolyze the dry matrix, the temperature was ramped and maintained at 400°C for 10 s. Temperature elevation to 1300°C generated a transient cloud of analyte vapor which was transported through a PTFE tube (45 cm×4 mm i.d.) into the quartz cell heated at 1000°C by the carrier gas stream (Ar 200 cm^3 min^{-1} and H$_2$ 70 cm^3 min^{-1}). The background corrected transient AA signal profile at 276.8 nm (Tl I) was recorded. The peak area was estimated synchronously with the integrator.

Results and Discussion

Optimization of instrument operating conditions

In order to avoid loss of thallium before the vaporization stage, moderate elevation of temperature throughout the heating cycle was essential. Experiments were carried out using 100 mm^3 aliquots containing 25 ng thallium(I).

A setting of 120°C for 210 s was suitable to obtain the required heating for drying.

The effect of ashing temperature on the atomic absorption of thallium was examined. An appreciable loss of thallium was observed at an ashing temperature of 600°C or above. Therefore, the ashing condition of 400°C–10 s was selected for the recommended procedure.

The effect of vaporization temperature with the maximum heating mode on the atomic absorption signal was optimized. The atomic absorption signal was maximum and constant over a temperature range of 1100 – 1500°C, and no background signal was observed. Thus, the vaporization temperature of 1300°C was chosen.

To prevent deterioration of the TBF and sample cuvette, hydrogen gas should be admitted to the argon gas; otherwise the tungsten reacts with oxygen, and the materials of TBF and cuvette become brittle. Subsequently, the effect of hydrogen gas flow rate was investigated in the range 0 – 150 cm^3 min^{-1}. Nearly maximum and constant atomic absorption was obtained when the hydrogen gas was introduced within the range of 50 – 100 cm^3 min^{-1}. However, at any flow rate below 30 cm^3 min^{-1}, vapor which was perhaps composed of tungsten trioxide from the boat material itself tended to appear. To obtain the boat durability as well as better sensitivity of thallium detection, the flow rate was controlled at 70 cm^3 min^{-1}. The enhancement of sensitivity by the hydrogen gas is probably due to its suppressive effect on the thallium oxide formation. Moreover, it is also due to the effect of elevating the temperature by burning hydrogen in the HQC.[8]

Regarding the flow rate of argon gas, an almost constant absorbance was obtained in the tested range of 100 – 600 cm^3 min^{-1}. Therefore, 200 cm^3 min^{-1} was selected as the optimum flow rate.

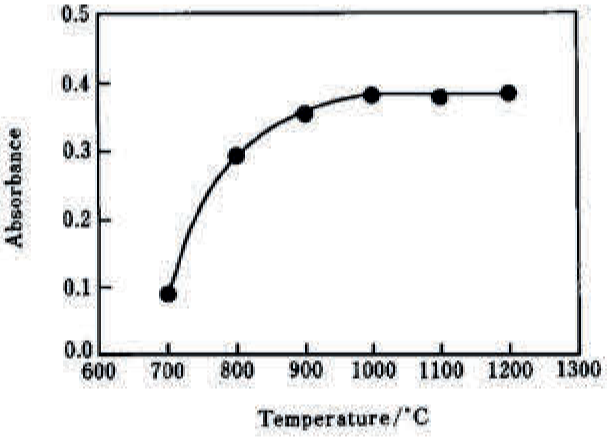

Fig. 1 Effect of the HQC temperature on the atomic absorption of thallium. Tl(I), 25 ng; Ar, 200 cm^3 min^{-1}; H$_2$, 70 cm^3 min^{-1}; vaporization temperature, 1300°C; ramp time, 0 s; ashing temperature, 400°C.

Table 1 Analytical results of some raticides

Sample	Thallium[a]/mg g^{-1}	
	Proposed method	ICPAES
Liquid type[b]	20.6±0.5	21.2±0.6
Solid type	4.0±0.3	3.8±0.1

a. Standard addition method, n=4.
b. Nominal value, 20 mg g^{-1}.

Figure 1 shows the effect of HQC temperature on the absorbance. When the temperature was set at 600°C, no peak was observed. The peak height increased with increasing HQC temperature up to 1000°C and remained constant over the range of 1000 – 1200°C. In this experiment, 1000°C was selected as the optimum HQC temperature.

Analytical performance

The limit of detection (3σ) was 0.43 ng (absolute amount of thallium). This amount corresponds to 4.3 ng cm^{-3} when a sample injection volume of 100 mm^3 is applied. If one takes a larger sample volume, a lower detectable concentration could be attained. For this purpose, repeated sample injections would be effective. The relative standard deviation for 10 replicate measurements of 10 ng thallium (100 mm^3) was 3.8%. The calibration graph was linear up to at least 80 ng thallium.

Application to practical samples

To establish the usefulness of this method, it was applied to the analyses of practical samples. However, since suitable certified reference materials were not available, commercially available raticides were analyzed. The digestion procedure was as follows: an aliquot of several grams of raticides was soaked in nitric acid overnight at room temperature, followed by heating at 150°C for about 4 h; then the content was diluted as required. In order to verify the analytical results obtained, parallel ICP-AES measurements were carried out for the same samples. As Table 1 shows, the results obtained by the proposed method are comparable with those by ICP-AES. Therefore, it may be said that the method can be effectively applied to the analyses of such samples.

In conclusion, since the analyte was separated from its inorganic matrix in order to introduce it into the atomic absorption spectrometer at a relatively low vaporization temperatures, no interference from most inorganic ions is expected. Therefore, the proposed method would be applicable to the determination of thallium even in complex matrices. Moreover, our method only requires several hundred micro-liters as a sample volume.

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