

Development of High Sensitivity Analysis of Micro-alloy in Steels by Mistral Desolvating Sample Introduction Method Hyphenated to ICP-MS/AES

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Abstract

Mistral Desolvation (MD), a sample introduction method for Inductively Coupled Plasma (ICP)-Atomic Emission Spectroscopy (AES) and Mass Spectrometry (MS), provides 5 times more sensitivity enhancement compared to the conventional method. When this method was applied to steel sample analysis, the mechanism of sensitivity enhancement was verified. The MD method provides a decrease of 100–250K plasma temperature, which leads to sensitivity loss. On the other hand, the desolvation process generates small droplets and sample transportation efficiency improves by a factor of 4.7 times, which is comparable to five-fold sensitivity enhancement. Thus, it is concluded that the dominant factor of sensitivity enhancement achieved by the MD method is improvement of sample transportation efficiency with decreasing droplet size. Moreover, the standard steel samples were analyzed by MD-ICP-AES. Sample consumption was reduced dramatically and sensitivity was improved with comparable precision compared to the conventional method. Therefore, application of this method to the chemical analysis of various micro-alloys in steels is expected.

1. Introduction

Faced with the demand for lighter-weight automotive steel sheets/plates, steel manufacturers are focusing on the development of high-strength steel sheets/plates with excellent formability. In such efforts, technologies to control micro-structure and precipitates in steel play an important role in terms of the design and development of new steel materials.¹⁾ In particular, micro-alloy to be added to steel significantly affects the mechanical properties of steel in the presence of elements in the form of precipitates or in the solid solution state, constituting one of the very important factors that need to be controlled.^{2,3)} Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) or Atomic Absorption Spectrometry (AAS) is widely used to obtain information on the components of micro-alloys in steel. However, it is not rare for steel manufacturers to need a concentration below the quantification limit of instruments used for these methods in the present day; the need to develop technologies for the sensitivity enhancement is thus growing.

On the other hand, Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS), which is more sensitive than ICP-AES and AAS by two to three orders of magnitude, has generally been used in infinitesimal analysis in an order of pg/mL to fg/mL in general fields outside the steel arena such as semiconductors, food, the environment, etc. When this is applied to steel analysis, separation and removal operation of the matrix is indispensable; and examples of the trace component analysis in steel have been reported wherein ICP-MS is combined with an ion exchange separation method^{4,5)}, emulsion separation method⁶⁾, solid-phase extraction separation method⁷⁾, and various other separation techniques^{8,9)}. However, simplification of the sample preparation procedure as well as further enhancement in the sensitivity of ICP-AES is still required in the on-site analysis.

Against such background, instrument manufacturers and research institutes are studying how to improve the sensitivity of ICP instruments. Particularly with respect to systems and methods for the sample introduction of ICP-MS and ICP-AES, in general, only

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about several percent of the total sample sprayed using a nebulizer is successfully introduced into plasma¹⁰. Furthermore, the signal/noise (S/N) ratio needs to be improved by selectively removing the matrix. There is room for sensitivity improvement, and a number of studies have been reported.¹¹⁻¹³

The mistral desolvation (MD) sample introduction method involves having the nebulizer-sprayed primary generated droplet group undergo a heating-cooling process to selectively remove the solvent components through the vaporization and condensation, thereby improving the sensitivity to several times higher than the sensitivity conventionally obtained.¹⁴ It is reported that the mechanism of sensitivity enhancement in this method is influenced by at least the following three hypotheses.

(1) Suppression effect in generation of a molecular ion species derived from a solvent¹⁵

The generation of polyatomic molecular ion species made up of target elements and solvent elements is suppressed by selectively removing solvents from sample droplets before the introduction to plasma, thereby increasing the amount of ions of the target elements.

(2) Influence of the change in the plasma state on the sensitivity¹⁶

When solvent vapors are removed by desolvation, hydrogen atoms in the plasma decrease. This leads to the lower electron density, lower heat conductivity in the plasma, lower plasma-to-sample energy transfer efficiency, and lower ionization temperature caused by all of the foregoing. As a result, the ionization peak position in the plasma and the ionization efficiency change, affecting the relative sensitivity, according to some reports. However, since the influence on the sensitivity depends on the instrument design, there is no unified view.

(3) Improving effect of the sample introduction efficiency¹⁷

Generally, ICP sample introduction systems are designed such that nebulizer-generated coarse droplets, which would adversely affect the stability of plasma, are removed beforehand in a spray chamber, and so only fine droplets are introduced to the plasma. Although they are removed beforehand in a spray chamber under the conventional introduction method, the desolvation is considered to cause such coarse droplets to become fine ones and to allow them to be transported to the plasma, thereby improving the sample introduction efficiency.

In this report, we describe the verification of the sensitivity enhancement mechanism of ICP-MS/AES using the above-described MD method and the contributing factor as revealed, and gained basic information for developing future sample introduction systems. Moreover, we describe the prospect of increasing the steel types to

which this method is applicable presented by the feasibility of sensitivity enhancement using a smaller sample consumption amount than that of the conventional method confirmed as a result of further examination for the application of this technique to the steel analysis.

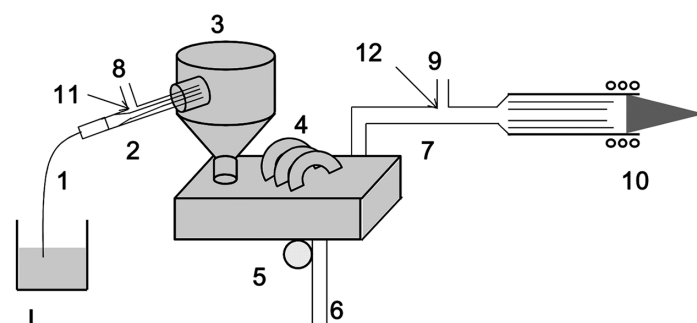
2. Experiments

Figure 1 is a schematic diagram of the MD sample introduction unit used in the tests called apex Q manufactured by Elemental Scientific Inc. For a nebulizer, a micro-flow nebulizer (PFA-400/100 nebulizer) was used. For a general-purpose sample introduction system, a cyclonic spray chamber (50 mL) and a concentric nebulizer (Conikal U-Series nebulizer; 1.0 mL/min) manufactured by Glass Expansion were used. For MD operating conditions, two levels of the heating temperature: 373 K and 413 K were set. The comparative verification under the condition without heating (at room temperature of 298 K) was performed, since the equipment design (type of nebulizer, spray chamber configuration, etc.) needed to be the same in order to examine the desolvation effects alone. The temperature of the cooler after heating was set to a constant 275 K.

In order to measure micro-alloying elements in the solution, an ICP mass spectrometer named Agilent 7500cs manufactured by Agilent Technologies Japan, Ltd. and an ICP emission spectrometer named ICPE-9000 manufactured by Shimadzu Corporation were used. In order to measure the sample uptake flow rate, a sample flow meter called TruFlo Sample Monitor manufactured by Glass Expansion was used. For the measurement of sample droplet size distribution, a cascade impactor called ELPI Classic manufactured by DEKATI was used. The Ar gas used in these tests was of 99.9995% purity.

Standard solution samples used in the test were prepared by adding a general-purpose multi-element standard solution (XSTC series manufactured by SPEX CertiPrep) and a general-purpose single-element standard solution (Assurance series manufactured by SPEX CertiPrep) such that high-purity nitric acid (TAMAPURE-AA100) manufactured by Tama Chemicals Co., Ltd. became 1%, and then making adjustment to a predetermined concentration using ultrapure water (Milli-Q, with resistivity of 18.2 M Ω and TOC of 8.0 ng/mL).

For the analysis of Japanese iron and steel certified reference materials for instrumental analysis, JSS154-9 and JSS158-1 were used. For the adjustment of the calibration curve solution, a metal standard stock solution (Cu, Ni, and V) manufactured by Kanto Chemical Co., Inc. was added to JSS-001 (high-purity iron), as a matrix, dissolved using hydrochloric acid (special-grade) also manufactured by Kanto Chemical to reach a predetermined concentra-



L: liquid sample; 1: PFA tube; 2: micro-flow nebulizer; 3: chamber with heater(373 K / 413 K); 4: cooler(275 K); 5: peristaltic pump; 6: drain; 7: PFA tube; 8: Ar carrier gas; 9: additional gas; 10: plasma torch; 11: carrier gas inlet; 12: additional gas inlet

Fig. 1 Schematic diagram of the MD instruments

tion, and adjusted to a constant volume with ultrapure water.

3. Experimental Results

3.1 Verification of the effect of suppressing the generation of solvent-derived polyatomic molecular ion species—Measurement result of the oxide-ion generation ratio in ICP-MS

A possible cause of sensitivity enhanced using the MD method is the suppression of oxide ion generation by solvent removal. As reported by Jakubowski et al., paying attention to Ce ions, which is one indicator of the oxide ion formation, oxide generation ratios (CeO⁺/Ce⁺) were compared at the MD heating temperatures of 298 K and 413 K.

In these experiments, 10 ng/mL of Ce standard solution (Assurance PLCE2 manufactured by SPEX CertiPrep, Inc.) was prepared and HNO₃ was added as a matrix to reach 1% of the solution. Using this solution, the amount of changes in the Ce oxide ion generation ratio was verified. The oxide ion generation ratios were calculated using the signal strength ratio between CeO⁺ (mass-to-charge ratio: *m/z*=156) and Ce⁺ (*m/z*=140). The result was 0.75% at 298 K (without heating) and 0.51% at 413 K (with heating). It was confirmed that the Ce oxide ion generation ratio was decreased slightly due to MD heating, but the decrease was very small at about 0.24%.

3.2 Examination of the effect on the sensitivity due to the change in the plasma state—Estimation results of the plasma temperatures by the Boltzmann plot method

It was assumed that the plasma temperature would rise due to the solvent removal effect of the MD method. In order to estimate the plasma temperature, the MD system was connected to the ICP-AES instrument and it measured the neutral atomic lines of Fe(I) using the ICP-AES from a Fe standard solution (Assurance PLFE2 manufactured by SPEX CertiPrep) adjusted to 1.0 μg/mL (matrix 1% HNO₃). Then, a Boltzmann plot from 13 different emission strengths was prepared (Table 1) and estimated the plasma temperature at each MD heating temperature. To prepare the Boltzmann plot, the following Boltzmann equation was used,¹⁸⁾

$$\log\left(\frac{I\lambda}{gA}\right) = -\frac{0.434E_n}{kT} + C \quad (C: \text{Constant}) \quad (1)$$

$$gA = \frac{8\pi^2 e^2}{mc} \cdot \frac{gf}{\lambda^2} \quad (2)$$

where *I*: emission strength, *λ*: wavelength, *g*: statistically weighted value of excited level, *A*: transition probability, *k*: Boltzmann constant, *T*: absolute temperature, *E_n*: excitation energy, *f*: oscillator strength, *e*: elementary charge, *m*: mass of electron, and *c*: velocity of light.

For emission strength *I*, the raw signal strength measured with the ICP-AES instrument was used. However, a relative plasma temperature comparison can be made without correcting the sensitivity coefficient of the equipment, since the experiments under the same equipment configuration and measuring conditions were conducted. Other parameters required for the calculation are cited from the NIST Atomic Spectra Database Lines Form¹⁹⁾. Strictly speaking, plasma temperatures must have differed, since the plasma source for ICP-AES used here differed from the plasma source for ICP-MS. However, it was considered that a relative comparison could be made by verifying the effect of heating temperatures of the MD system using the same plasma source in these experiments.

The heating temperature of the MD system was changed between three levels and compared the difference in plasma tempera-

Table 1 Measured Fe(I) emission lines and energy transition

Wave length <i>λ</i> (nm)	<i>E_k</i> (eV)	Lower level	Upper level	<i>gA</i>
370.925	4.257	3d ⁷ (⁴ F).4s	3d ⁷ (⁴ F).4p	1.09E+08
371.993	3.333	3d ⁶ .4s ²	3d ⁶ (⁵ D).4s.4p.(³ P ^o)	1.78E+08
372.256	3.417	3d ⁶ .4s ²	3d ⁶ (⁵ D).4s.4p.(³ P ^o)	2.48E+07
372.762	4.284	3d ⁷ (⁴ F).4s	3d ⁷ (⁴ F).4p	1.12E+08
373.332	3.431	3d ⁶ .4s ²	3d ⁶ (⁵ D).4s.4p.(³ P ^o)	1.94E+07
373.486	4.178	3d ⁷ (⁴ F).4s	3d ⁷ (⁴ F).4p	9.91E+08
373.713	3.369	3d ⁶ .4s ²	3d ⁶ (⁵ D).4s.4p.(³ P ^o)	1.27E+08
374.826	3.417	3d ⁶ .4s ²	3d ⁶ (⁵ D).4s.4p.(³ P ^o)	4.58E+07
374.949	4.221	3d ⁷ (⁴ F).4s	3d ⁷ (⁴ F).4p	6.87E+08
375.823	4.257	3d ⁷ (⁴ F).4s	3d ⁷ (⁴ F).4p	4.44E+08
376.379	4.284	3d ⁷ (⁴ F).4s	3d ⁷ (⁴ F).4p	2.72E+08
376.554	6.529	3d ⁷ (² H).4s	3d ⁷ (² H).4p	1.43E+09
381.584	4.734	3d ⁷ (⁴ F).4s	3d ⁷ (⁴ F).4p	7.84E+08

^o: Odd parity

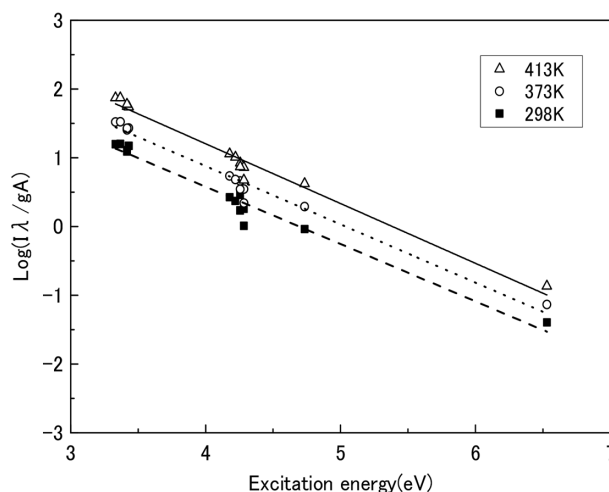


Fig. 2 Boltzmann plot upon heating temperature of MD process

ture between the three MD heating temperatures. Figure 2 shows a Boltzmann plot of the MD heating temperatures. Since sufficient linearity was obtained at any of the temperatures, with correlation coefficient *R* of about 0.97 to 0.98, we calculated plasma temperature *T_p* from the slopes of the straight line (Fig. 3).

As a result, it was confirmed that the plasma temperature under each heating condition was around 6000 K. Also noted was a tendency of the plasma temperature to drop about 100 K to 250 K along with the increase in the MD heating temperature, which is contrary to expectations.

3.3 Examination of improvement effect of the sample introduction efficiency—Calculation result of the sample introduction efficiency by the cascade impactor

It is possible that the solvent removal effect of the MD method causes the size of each droplet to decrease and leads to an increase in the amount of fine droplets. It was assumed that the absolute amount of fine droplets with diameters smaller than the cut-off diameter of the spray chamber (assumed to be about 10 μm) would increase, and more droplets would be introduced to the plasma.

In order to verify changes in the droplet size distribution, droplets of the 50 μg/mL Ce standard solution transported from the outlet

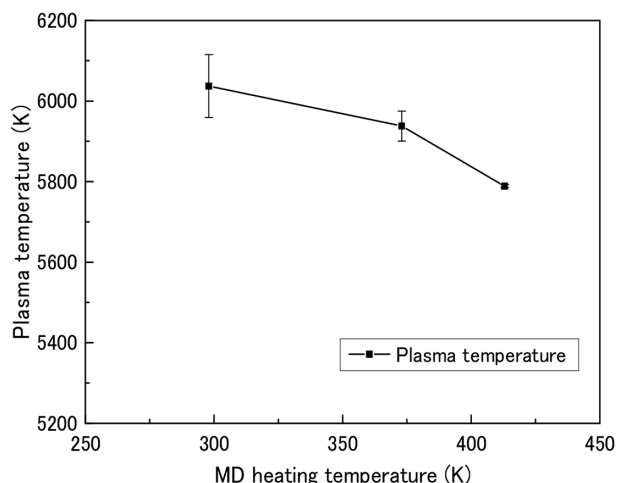


Fig. 3 Results of plasma temperature assumption upon heating temperature of MD process

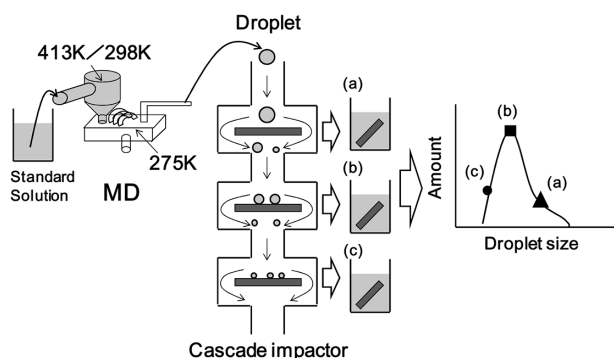


Fig. 4 Experimental procedure of the size distribution analysis of sample droplets by using cascade impactor

of the MD system were directly sampled in each droplet size by the cascade impactor, and each size of the droplets was collected on the filter for a period of 30 minutes (Fig. 4). Then, the element (Ce) in the droplets caught on the filter was collected again in the 1% HNO₃ solution, the solution was adjusted to a set volume, and an ICP-MS quantitative analysis was performed, comparing the droplet size distribution and sample transportation efficiency.

For this experiment, the influence of the nebulizer performance, spray chamber configuration, and droplet transportation paths were excluded, and the droplet size distribution by changing only the heating temperature of the MD system was compared between 298 K and 413 K in order to simply verify the desolvation effect (Fig. 5). As a result, it was revealed that the total content of Ce in droplets which were smaller than the cut-off diameter of the spray chamber substantially increased after the MD heating. Also, the average diameter of droplets was 0.26 μm at 298 K and 0.41 μm at 413 K, showing an insignificant change.

The average size of these droplets will vary depending on the type of the nebulizer used, flow rate of Ar carrier gas, sample uptake rate, and other measurement conditions.^{20, 21)} In this study, it was found that the relative tendencies are the same, although strict comparison is not possible because of the difference in the measuring conditions and particle size measurement methods, such as the use of a cyclone-type chamber and measurement of the cut-off diameter of the cascade impactor.

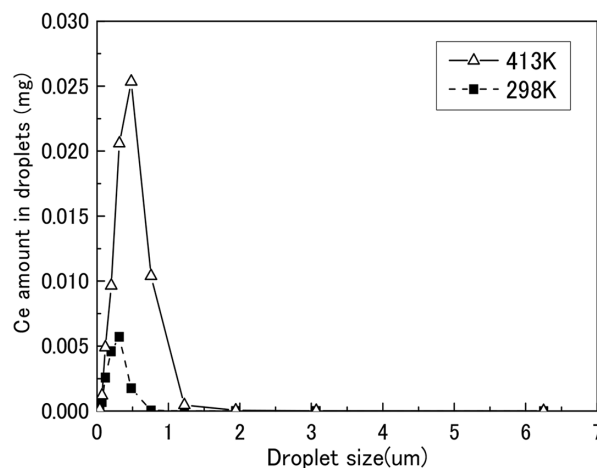


Fig. 5 Droplet size distribution upon heating temperature of MD process

Furthermore, the sample introduction efficiency was defined as Eq. (3) and the MD system heating temperatures of 298 K and 413 K were compared. It was revealed that the sample introduction efficiency improved approx. 4.7 times from 2.6% to 12.1%, a clear indication of the difference in the amount of droplets between with or without desolvation.

Sample introduction efficiency (%)

$$= \frac{\text{Amount of collected sample by CI}}{\text{Amount of uptaken sample}} \times 100 \quad (3)$$

3.4 Analysis results of Japanese iron and steel certified reference materials for instrumental analysis

Finally, an MD-ICP-AES analysis was applied to Japanese iron and steel certified reference materials (CRMs). The measurement samples were prepared in the following steps. Firstly, 20 mL of HCl were added to the weighed 0.5 g Japanese Iron and Steel Certified Reference Materials shown in Table 2. The resulting mixture was heated at 200°C to completely dissolve the sample, and then the volume was adjusted to 200 mL. The standard solution was prepared as follows. Namely, similarly to above, 0.5 g of high purity iron (JSS001-6) were thermally decomposed with 20 mL of HCl at 200°C, and after the standard solution of Cu, Ni, and V was added so as to give the concentrations of 0 to 30 μg/mL, the volumes were adjusted to 200 mL. The sample preparation described above was independently conducted twice in parallel and measured with MD-ICP-AES.

Table 3 shows the quantification results of the CRMs using the MD-ICP-AES method. In each case of Cu, Ni, and V, the obtained results were favorably consistent with the certified values. These results confirm that the use of this analytical technique was capable of providing precision equivalent to the conventional ICP-AES method.

Moreover, the calibration curves of the MD method and a conventional sample introduction method (combined use of a concentric nebulizer and a cyclone-type chamber) were compared. The result is shown in Fig. 6.

It was revealed that with the MD method, the slope of the calibration curves improved about three-fold on average under the condition of co-existence of the iron matrix. Although only the Cu calibration curve is shown here, the other elements showed almost the same results. In addition, while the sample uptake amount was 1 020 μL/min when using the conventional concentric nebulizer, it was 116 μL/min when using the micro-flow nebulizer of the MD method,

Table 2 Certified values of CRMs

JSS No.	JSS154-9	JSS158-1	JSS001-6
C	0.11	0.14	0.00024
Si	0.60	0.30	0.0001
Mn	1.15	0.47	0.000003*
Ni	0.52	0.048	0.00002*
Cu	0.20	0.16	0.000036
V	0.30	-	<0.00003*
P	0.0045	0.006	0.00005*
S	0.0045	0.007	0.00015
Cr	1.98	0.042	<0.00006*
Mo	0.37	-	<0.00002*
Al	0.009	-	<0.0001*
N	0.0117	-	0.00021
Co	-	0.30	0.000032
Ti	-	0.10	<0.00002*
As	-	0.092	<0.0003*
Sn	-	0.050	0.00003*
Nb	-	0.088	<0.00003*
B	-	-	0.00002*
Ca	-	-	<0.0002*
Mg	-	-	<0.00006*
Pb	-	-	0.000018
W	-	-	0.00001*
Zn	-	-	0.00019

Asterisk mark is attached on reference value.

Table 3 Analytical results of CRMs by MD-ICP-AES

(a) JSS154-9		unit: mass%		
n	Cu	Ni	V	
n=1	0.195	0.519	0.294	
n=2	0.201	0.533	0.300	
Average	0.198	0.526	0.297	
Certified value	0.200	0.520	0.300	

(b) JSS158-1		unit: mass%	
n	Cu	Ni	
n=1	0.159	0.049	
n=2	0.163	0.050	
Average	0.161	0.050	
Certified value	0.160	0.048	

constituting only 11.4% of the conventional method.

4. Discussion

Described below are our considerations on the experimental results corresponding to the three hypotheses described in Chapter 1 regarding the causes of the sensitivity enhancement produced by the solvent removal of MD, as well as the applicability to the analysis of steel.

4.1 Suppression effect in generation of a polyatomic molecular ion species derived from a solvent

As the primary cause, the oxide ion generation suppression effect of solvent removal is suggested. The proposed theory is that the solvent (water in this study) in droplets evaporates inside the MD

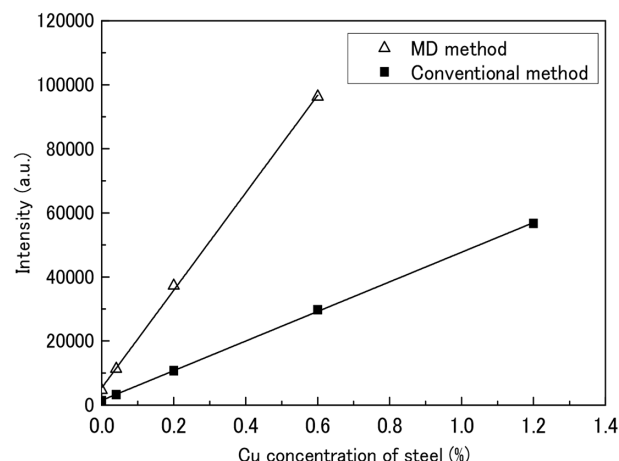


Fig. 6 Comparison of Cu (213.598 nm) calibration curve between MD and conventional sample introduction system

system to be separated from the droplets, condenses in the cooler to be selectively removed, leading to a decrease in the total amount of the solvent that reaches the plasma. This suppresses the reaction between O₂ contained in the solvent (water) and the element to be analyzed, reduces oxide ions, and leads to the generation of more ions of the target element for analysis.

The results of the experiments have confirmed that the MD heating slightly reduces the oxide ion generation ratio by 0.24%. Zhu and Browner²²⁾ and Jakubowski et al. also reported a comparable effect of desolvation to reduce the oxide ion generation ratio. If a heater is provided, the amount of solvent vapors transported to the plasma will increase and a large amount of oxide ions will be generated compared with the conventional method. Therefore, the removal of solvent vapors using a cooler is considered essential in order to reduce oxide ions.

Regarding the relationship between the oxide ion generation suppression effect and sensitivity improvement, although there have been no in-depth reports in the past on the matter, in view of any of the reductions in the oxide ion generation ratios that were extremely small, the oxide ion generation suppression effect alone is not sufficient to explain the five-fold or more improvement in the sensitivity. Based on the above, it is suggested that the main causes of the sensitivity enhancement using the MD method are attributable to other factors.

4.2 Effect on the sensitivity due to the change in the plasma state

As the secondary cause, the effect of changes in the state of plasma as a result of the solvent removal is suggested. In order to confirm changes in the plasma state due to a decrease in hydrogen atoms in the plasma caused by desolvation, the plasma temperature was estimated using the Boltzmann plot using ICP-AES.

The results of the experiments revealed a tendency of the plasma temperature decreasing about 2°C along with the MD heating temperature rise by 1°C. This is consistent with information obtained in the past¹⁶⁾. The following paragraphs describe our considerations on the reason for the tendency.

The decrease in the plasma temperature can be explained well, if it is assumed that when the MD heating temperature was raised, the solvent in droplets evaporated, diminishing the droplets in size, increasing the absolute amount of fine droplets with diameters smaller than the cut-off diameter of the spray chamber, and also increasing the total amount of droplets per unit time introduced to the plasma.

In other words, as the heating temperature of the MD system was raised, the total amount of droplets introduced to the plasma increased, lowering the plasma temperature. Incidentally, since during these experiments the temperature of the cooler was fixed at 275 K, and as Jakubowski et al. reported, 80% or more of the water content that evaporated after the desolvation at the heater is presumably condensed at the cooler in the later stage and sent to the drain, and the effect of the cooler on the plasma temperature is considered negligible.

There have been no in-depth considerations in past reports on changes in the plasma temperature and changes in the sensitivity. Still, it was thought that the plasma temperature did not significantly change and that the effect on the sensitivity enhancement was small because these experiments were conducted with a constant cooling temperature.

4.3 Improving effect on the sample introduction efficiency

As the tertiary cause, it is suggested that the amount of fine droplets increases along with the decrease in the size of overall droplets due to the solvent removing effect of the MD method. Normally, when a solution sample is sprayed using a nebulizer, droplets in a wide size range are formed. The conventional method has a design that reduces the solvent load and stabilizes the plasma by introducing only fine droplets selected beforehand from the sprayed sample in the spray chamber. Making droplet sizes fine by desolvation is considered to allow more droplets to be introduced to the plasma, improving the sample introduction efficiency and enhancing the sensitivity.

The droplet size measurement results have revealed that the MD system heating causes the absolute amount of droplets with diameters smaller than the cut-off diameter of 10 μm of the spray chamber to significantly increase, while the average droplet size hardly changed. The measured droplets were those that constituted droplets that passed through the spray chamber and were actually introduced into the plasma. Since the MD system heating increased the overall amount of droplets of 10 μm or smaller in diameter, it is considered that droplets that were removed in the spray chamber and not measured under the conventional method were desolvated and made smaller than 10 μm, and measured.

It was also demonstrated that the MD system heating improved the sample introduction efficiency by approx. 4.7 times and that there was an increase in the amount of droplets introduced. This is roughly consistent with the report by Hartley et al. on slurry sample introduction. The sensitivity enhancement effect of Ce using ICP-MS was 4.6 times, which is equivalent to the improvement in the sample introduction efficiency achieved using the MD system heating. Therefore, the improvement effect on the sample introduction efficiency is considered to contribute to the sensitivity enhancement most effectively (Table 4). As mentioned earlier, according to Jakubowski et al., the effect of cooling alone is considered to re-

move most of the solvent vapor, and sufficiently improves the influence of the polyatomic molecular ion generation ratio and the plasma temperature. Thus, it is considered that the largest cause of the sensitivity enhancement shown when heated under the MD method is the sample introduction efficiency improvement effect.

4.4 Effect of the MD method used for analysis of steel

Next, the analysis results of CRMs using the MD-ICP-AES method are considered. In view of the sample uptake amount of a micro-flow nebulizer used for the MD method, which is about one ninth of a concentric nebulizer used for the conventional method, it is assumed that a similar decrease in the sensitivity would occur.

Using the same cyclone-type chambers, the sensitivity of these two nebulizers was compared. The result clearly showed that as compared with the nebulizer used for the conventional method, the relative detection sensitivity decrease of the micro-flow nebulizer was suppressed to 42%, considerably lower than the predicted 88.6% (Fig. 7).

This is possibly due to the spray efficiency of the nebulizer. In other words, the micro-flow nebulizer is superior to the conventional concentric nebulizer in effectively generating fine droplets, which contributes to the improvement of the sample introduction efficiency to plasma.

The amount of transported samples increases about 4.7 times due to the solvent removal of the MD method. Assuming that the relative detection sensitivity under the conventional method (using a concentric nebulizer and a cyclone-type chamber) is 1.0, the sensitivity under the MD method is estimated to be $(1.0 - 0.42) \times 4.7 \approx 2.7$ times, which is roughly consistent with the 3.0 times as measured. Given this, it is concluded that by combining a micro-flow nebulizer and the MD method's desolvation process and under the condition that the sample consumption is limited to about one ninth of the conventional amount, the detection sensitivity can be improved by three times or more.

Based on the above, by applying this method to the analysis of steel, the conventionally required amount of the dissolved sample, which is generally 0.5 g, can be reduced to one twenty-seventh (about 18 mg). In addition, the micro-flow nebulizer used for the MD method has the same spray system as that of nebulizers in the conventional method, and does not have the problem of contamination or blockage by an iron matrix, contrary to ultrasonic nebulizers with excellent introduction efficiency. Furthermore, the difference in

Table 4 Experimental results and influence for ICP sensitivity

	Our results	Influence for sensitivity
1. Inhibition of poly-atomic ion generation	Approximately 0.2% reduced	Slightly effective
2. Plasma temperature change	100–250 K reduced	Slightly negative
3. Improvement of sample transportation efficiency	Almost 4.7% improved	Most effective

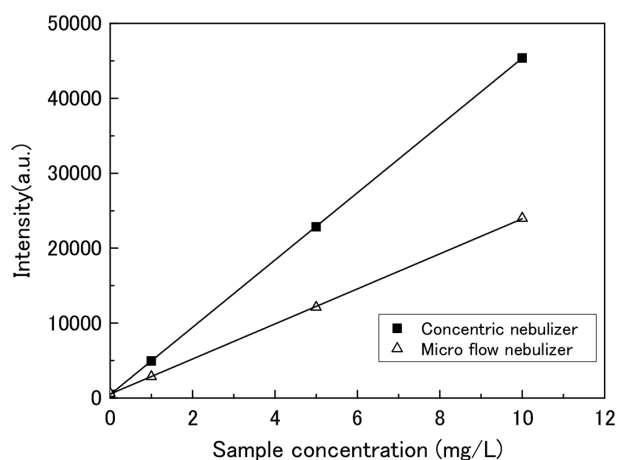


Fig. 7 Comparison of sensitivity between concentric nebulizer and micro flow nebulizer measuring Cu 327.396 nm emission line

detection sensitivity can be explained solely by the difference in sample introduction efficiency as described above. For these reasons, no influence of coexisting iron matrices has been observed on the matrix effect. For example, the use of this method allows high-sensitivity analysis of defective and corroded parts of steel materials by regulating sample consumption, even when only a few to a dozen mg of samples can be taken and only a small amount of the dissolved sample is available for measurement. So, not only analyzing micro-alloy contained in steel materials, the MD method is also likely to simplify the sample preparation techniques, improve the quantification limit, and make other contributions to broadening the steel chemical analysis application by ICP-AES.

5. Conclusion

This article described the considerations on the sensitivity improvement mechanism obtained when the MD method is used with ICP-MS/AES and the three factors that assumedly involve the mechanism.

- (1) A slight decrease (0.24%) in the ICP-MS oxide ion generation ratio caused by the heating process of the MD method was confirmed.
- (2) The ICP plasma temperature estimated using the Boltzmann plot method was about 6000 K. The plasma temperature decreased by approx. 100 to 250 K as the MD method chamber heating temperature rose.
- (3) The MD method caused droplet sizes to be finer, increasing the amount of droplets with diameters smaller than the cut-off diameter of the spray chamber (about 10 μm). Thus, the sample transportation efficiency of droplets was increased to approx. 4.7 times.

These findings have confirmed that the sample introduction efficiency improvement effect that the fine droplets have is the dominant factor of the sensitivity improvement mechanism involved in the MD method.

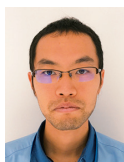
Furthermore, the MD method analysis results of Japanese iron and steel certified reference materials for instrumental analysis use

have revealed that the MD method is capable of reliable and accurate measurement in a manner adequately consistent with the certified values, and that even under the condition of a reduced amount of sample consumption to one ninth, a three-fold increase in the sensitivity is allowed. This suggests that the sample amount to be dissolved can be cut to about one twenty-seventh of the amount conventionally dissolved.

These findings offer the broadening of prospects of the analysis object range by combining suitable types of nebulizers with the MD method in the course of the research and development of analysis technologies for higher sensitivity and more accurate detection of micro-alloys contained in steel materials.

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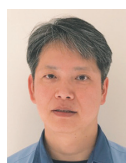
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