Comparison of Matrix Modifier for the Determination of Aluminum in Seta River Water by Graphite Furnace Atomic Absorption Spectrometry with Polarized Zeeman Background Correction

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Abstract

Four different compositions, i. e., a mixture of magnesium and palladium nitrate, magnesium nitrate, palladium nitrate both dissolved in nitric acid, and magnesium nitrate dissolved in pure water, were examined at high (1000ppm) and low (100ppm) concentrations for the suitability as the matrix modifier for the determination of aluminum in Seta River water. For the determination, the standard addition method was employed and the slopes of the graph calculated by the peak－height mode and the peak－area mode were compared to those of pure water. The chemical interference, evaluated as the ratio of these slopes, was smaller in the peak－area mode except for the 100ppm palladium. The matrix modifier solutions containing palladium have a tendency to shorten the life of a pyrocoated graphite cuvette. The peak profile from the matrix modifiers containing nitric acid was often distorted at the initial rising part. We concluded that magnesium nitrate dissolved in pure water (1000ppm) was the most appropriate matrix modifier for the determination of aluminum in Seta River water from among the tested modifier solutions, although the chemical interference was not completely removed.

Key words : GFAAS, Aluminum, Standard addition, Matrix modifier, Magnesium nitrate, Palladium, Seta River water

Although aluminum is the third most abundant element in the earth's crust, its concentration in environmental water is usually very low when it is neutral or slightly alkaline pH because of the low solubility of aluminum in this pH region.[1] The determination of aluminum according to its chemical form is regarded to be important not only because of the relevance to the toxic properties of aquatic life, but also to human health. For example, a positive correlation has been reported between the concentration of aluminum in drinking water and the rate of people who suffered from Alzheimer's disease.[2]

Graphite furnace atomic absorption

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spectrometry (GFAAS) has been frequently used for the determination of aluminum in environmental water, because it has a sensitivity high enough to analyze such samples.

We have been studying the speciation of aluminum in rain water[3] and river water[4–6] using cation–exchange chromatography with fluorometric detection of the aluminum–lumogallion complex. In 2001, a Hitachi GFAAS with Zeeman background correction (Z 5710) was introduced at Shiga University. For the determination of aluminum by the GFAAS, we first used a magnesium nitrate matrix modifier according to the instruction manual (Part No. 172 – 9110 – 1 TH–F) provided by the manufacturer. We examined the influence of the signal operation mode on the determination of aluminum in Seta River water using the standard addition method.[7] With respect to accuracy, it was concluded that the integrated absorbance (peak–area) mode was better than the peak absorbance (peak–height) mode which was originally adopted as the default mode by the manufacturer. However, the slope of the standard addition graph for the Seta River water was always smaller than that for pure water in both signal operation modes. The difference in the slope implied the existence of a chemical interference.

In order to determine the modifier that can suppress the chemical interference, we initially tested some other modifiers such as calcium nitrate or nickel nitrate, because they were recommended in the literature.[8, 9] However, they did not produce a good result.

In the literature, various matrix modifiers have been used. Magnesium nitrate was introduced in the earlier stage and may be the most popular for the

determination of aluminum.[10–16] Styris and Redfield examined the mechanism of action and stated that magnesium inhibited the formation of gaseous $Al(OH)_2$, consequently, the low–temperature loss of aluminum was inhibited.[17, 14]

The mixture of magnesium nitrate and palladium nitrate was also used in some studies.[18–20] Palladium alone was also used for the determination of aluminum.[21] Other modifiers have been used for the determination of aluminum in various kinds of samples.[22–32] Nitric acid without any metals was sometimes used instead of a metal matrix modifier.[33–35]

In 2003, Hitachi began to provide two kinds of matrix modifiers, i. e., magnesium nitrate dissolved in nitric acid and a mixture of magnesium nitrate and palladium nitrate dissolved in nitric acid. The former was intended to be used for the determination of aluminum and the latter was for the determination of As, Se, Pb, Sn, Cd, and Cr. Because Bermejo–Barrera et al. recommended the magnesium and palladium nitrate mixed modifier for the determination of aluminum,[18] we tried to use it.

In this study, we examined the suitability of matrix modifiers for the determination of aluminum in Seta River water. Not only the two modifiers provided by Hitachi, but a palladium modifier were also used for the purpose of comparison. Because the two different concentrations, i. e., 1000 ppm and 100 ppm, were used by the Hitachi modifiers, we also used these two concentrations. As for the magnesium nitrate modifier, the effect of nitric acid was also examined.

Experimental

Reagents.   Ultrapure   water   was

prepared from once-distilled water using a Millipore Milli-Q Labo system. Ultrahigh-purity nitric acid was purchased from Tama Chemicals (Kanagawa, Japan) as Tamapure AA-100. As the matrix modifier, magnesium nitrate, a mixture of magnesium and palladium nitrate, and palladium nitrate were used. Magnesium nitrate hexahydrate (Suprapur® grade) was purchased from Merck (Darmstadt, Germany). In order to evaluate the effect of nitric acid in the modifier, we prepared two types of magnesium nitrate modifiers, which was dissolved into ultrapure water and diluted nitric acid. These solutions were abbreviated as Mg and Mg/HNO_3. A mixture of magnesium and palladium nitrate dissolved in nitric acid (abbreviated as Pd+Mg) was purchased from Hitachi (Tokyo, Japan) and the Kanto Chemical Co., Inc. (Tokyo Japan). Palladium nitrate dissolved in nitric acid (abbreviated as Pd) was also obtained from the Kanto Chemical Co., Inc. These reagents were originally prepared as a matrix modifier of GFAAS. We noted that the Mg+Pd modifier purchased from Hitachi was produced by the Kanto Chemical Co., Inc. The original solutions of the Pd+Mg and Pd matrix modifiers were diluted to 1000 ppm and 100 ppm by the addition of nitric acid, respectively. Table 1 lists the matrix modifiers.

A stock aluminum standard solution (10^{-2} mol dm^{-3}) was prepared by dissolving 0.4744 g of $AlK(SO_4)_2 \cdot 12 H_2O$ into 0.1 dm^{-3} of 10^{-3} mol dm^{-3} nitric acid. The aluminum standard solutions (0, 0.2, 0.4, 0.6, 0.8 and 1.0 μmol dm^{-3}) were prepared by serial dilution of the stock solution. The pH of the standard solutions was adjusted to 4.0 by adding nitric acid. These solutions were kept in a plastic volumetric flask after their preparation.

Apparatus. A Model Z 5710 Hitachi polarized Zeeman graphite furnace atomic absorption spectrometer (GFAAS) equipped with an autosampler was used. A pyrolytic graphite cuvette (type A) was used for the wall atomization. Argon gas of 99.99 % purity was used. The instrumental conditions were the same for all the modifiers and are summarized in Table 2. For the signal operation mode, the peak-height mode and the peak-area mode were used for the purpose of comparison.

Sample and its treatment. The Seta River water was sampled on the west side of the river near the Shiga-Dai Mae bus stop and filtered within one hour using a 0.45 μm membrane filter (Type HAWP, Millipore, USA). The filtered river water was kept in a thermostated bath at 30℃ and used within one month.[5]

Determination of aluminum. The standard addition method was used throughout. For atomization, 10 μL of an aluminum standard solution, 10 μL of a sample and 5 μL of a matrix modifier were injected into a cuvette by the autosampler.

Table 1   List of the matrix modifiers

No.	Composition	Concn. of metal/ppm	Concn. of nitric acid/mol dm^{-3}
1	(Pd+Mg)/HNO₃	100	1.52
2	(Pd+Mg)/HNO₃	1000	1.75
3	Mg/HNO₃	100	1.49
4	Mg/HNO₃	1000	1.49
5	Mg	100	0
6	Mg	1000	0
7	Pd/HNO₃	100	1.52
8	Pd/HNO₃	1000	1.75

The Seta River water sample was measured together with pure water in order to compare the slope of the graph as a measure of chemical interference. The baseline of the blank data was always corrected using the software provided by the manufacturer. Because the function of the correction software was so primitive that the baseline could only be moved vertically, an accurate correction was rather impossible. The measurements were repeated three times and their mean value was used for the calculation. Any abnormal data were omitted. We tried to use the data only in the linear part of the standard addition graph. The concentration of aluminum was calculated from the regression line of the standard addition graph, in which at least three points including the point of the lowest concentration were used.

Results and Discussion

Instrumental conditions. In a previous paper,[7] we slightly modified the instrument conditions given by the instruction manual. In order to prevent bumping, the drying temperature was lowered from 80℃ to 60℃ and kept at 60℃ for 100 s. Also, the pyrolysis temperature was raised from 700℃ to 1100℃. The instrumental conditions are summarized in Table 2. These conditions are same as in a previous paper.[7] In order to determine the suitability of these instrumental conditions for the other modifiers, the effect of the pyrolysis and atomization temperatures was examined using the Seta River water and the 0.6 μmol dm^{-3} aluminum standard solution, while the other conditions were unchanged. The peak−height instead of the peak−area was chosen as a measure of the instrument response, because the peak became too broad to use for the determination under some conditions.

Figure 1 shows the results for the 0.6 μmol dm^{-3} aluminum standard solution. Figure 2 shows the results of the Seta River water. It should be noted that the sample solution used in the pyrolysis experiment may be different from that used in the atomization experiment with the same modifier. Thus, it is impossible to compare the peak−heights in the pyrolysis and atomization graphs even if the same modifier was used. The peak−height in these figures was the net absorbance which was obtained by subtracting the blank absorbance of pure water from the original peak−height of a sample. Therefore, the negative absorbance that appeared in the

Table 2   Instrument conditions and furnace program for the measurement of aluminum by GFAAS

Instrument conditions				
Wavelength		309.3 nm		
Lamp current		12 mA		
Slit width		1.3 nm		
Type of cuvette		Pyrolytic tube A		
Background correction		Polarized Zeeman		
Furnace program				
Step	Temperature/℃	Ramp/s	Hold/s	Argon−gas flow/cm^3 min^{-1}
1 Dry	60	0	100	200
2 Ash	1100	15	25	200
3 Atomize	2700	0	4	30
4 Clean	2800	0	4	200
5 Cool down	—	0	20	200

(a) (●) 100ppm Pd+Mg , (○) 1000ppm Pd+Mg

(b) (●)100ppm Mg+HNO₃, (○) 1000ppm Mg+HNO₃

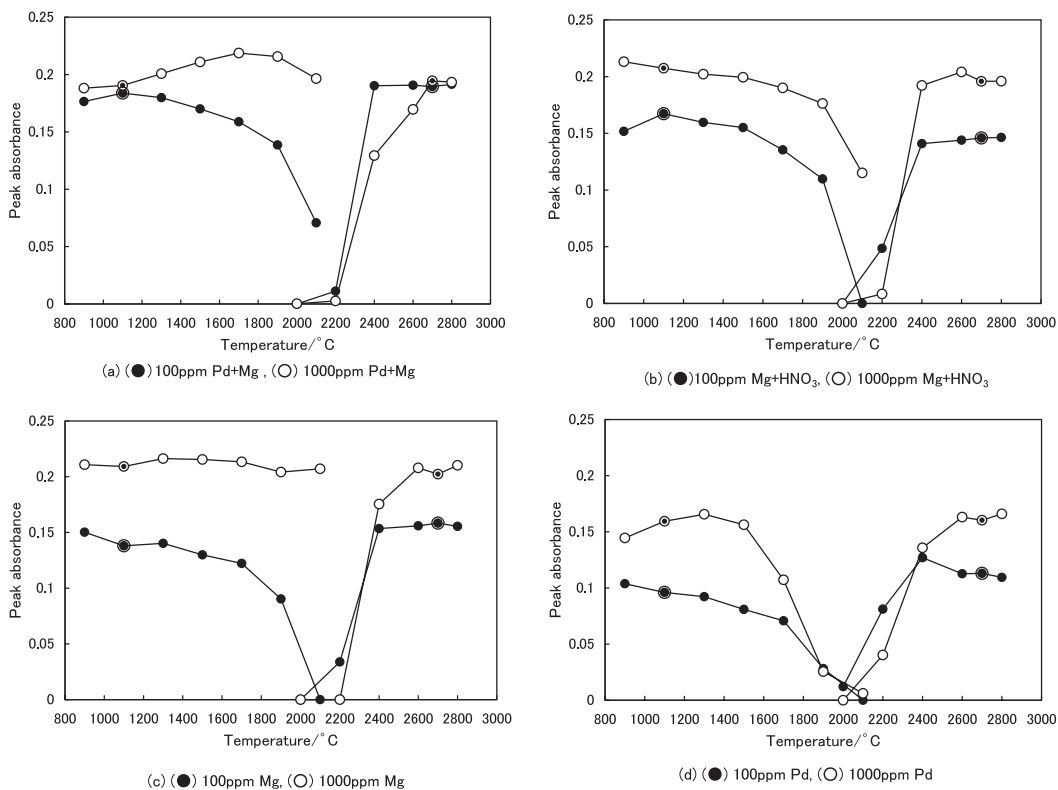(c) (●) 100ppm Mg, (○) 1000ppm Mg

(d) (●) 100ppm Pd, (○) 1000ppm Pd

Figure 1   Effect of pyrolysis and atomization temperature on the absorbance of $0.6\,\mu$mol dm^{-3} aluminum standard solution.   The pyrolysis temperature and atomization temperature were kept at 1100℃ and 2700℃, respectively, when one of the two factors was changed.

atomization graph d of Figure 2 does not mean a negative peak. Under this condition, the peak height of the pure water happened to be higher than that of the sample.

There are several differences in the pyrolysis and atomization graphs for the aluminum standard solution and Seta River water. For example, the peak–height in the pyrolysis graph for the 1000 ppm modifiers (No. 2, 4, and 6 as shown by the open circles in graph a, b, and c) at 2100℃ was very small in the Seta River water, while the corresponding absorbance was relatively high in the aluminum standard solution. The peak–height in the atomization graph for the 100 ppm modifiers (No. 1, 3, and 5 as shown by the closed circles in graph a, b, and c) at 2200℃ was fairly high in the Seta River water, while the

corresponding absorbance was rather low in the aluminum standard solution. These examples indicated that the atomization of aluminum occurred at a relatively low temperature in the Seta River water probably due to the chemical interference by chloride and so on.

However, the selected pyrolysis and atomization temperatures (1100℃ and 2700 ℃) were suitable for intercomparison of the modifiers.

Standard addition graph. Figure 3 shows an example of the standard addition graphs versus both signal operation modes. In the graphs for the Seta River water (shown by the open circle), the regression lines were drawn using the mean value of the three measurements for every concentration. On the other hand, the

(a) (●)100ppm Pd+Mg , (○) 1000ppm Pd+Mg

(b) (●)100ppm Mg+HNO$_3$, (○) 1000ppm Mg+HNO$_3$

(c) (●) 100ppm Mg, (○) 1000ppm Mg
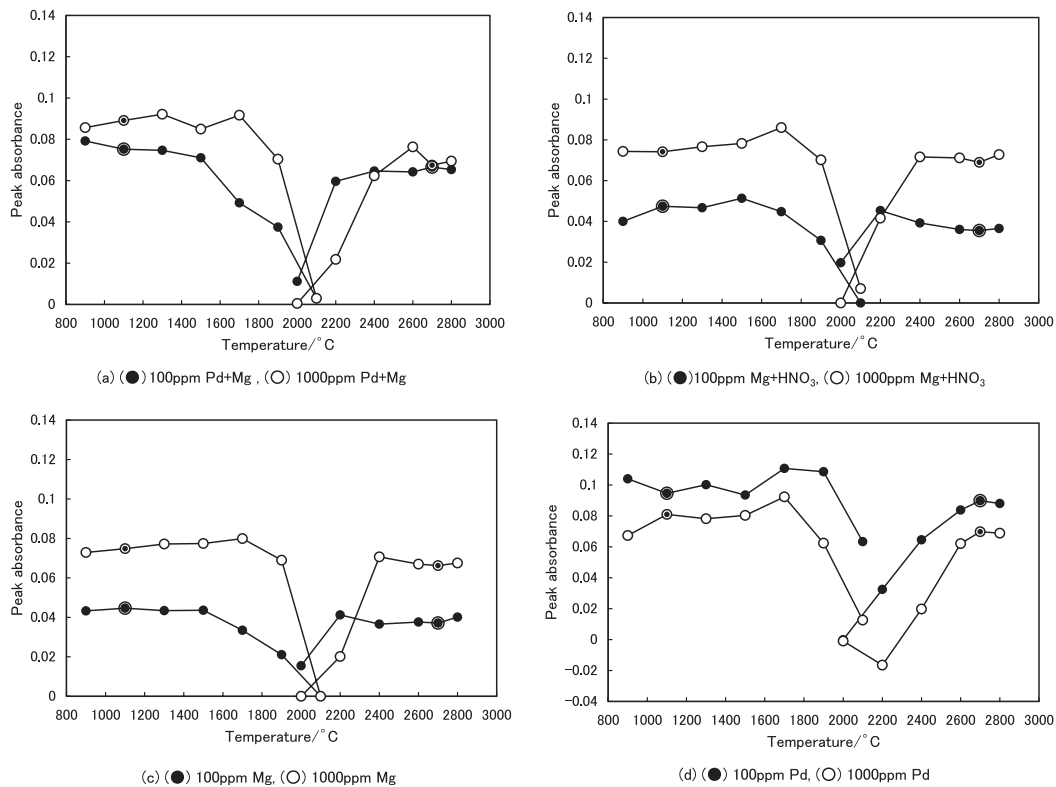
(d) (●) 100ppm Pd, (○) 1000ppm Pd

Figure 2　Effect of pyrolysis and atomization temperature on the absorbance of the Seta River water. (Each graph was obtained using one sample, but the sample used for the pyrolysis and atomization temperature experiment was not always the same.)
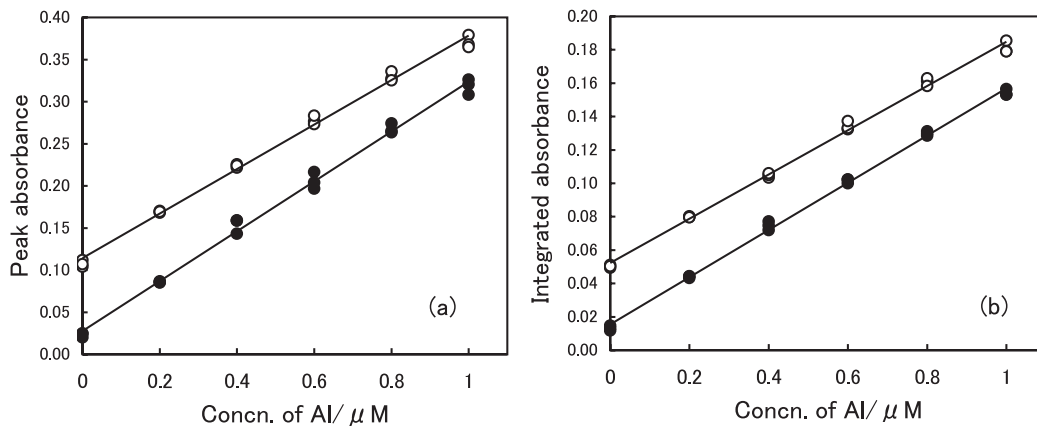

Figure 3　Standard addition graphs for the Seta River water(○) and pure water(●) versus the two signal operation modes. The Seta Rive water was sampled on March 8, 2006. The matrix modifier no. 6 was used. Three repeated measurements were performed in a certain experimental condition.

point at 0.4 μmol dm^{-3} was omitted in the graphs for the pure water (shown in the closed circle), because the correlation was improved.　We used at least three data points to construct the regression line even if some data points were omitted in order to improve the correlation.　The obtained slope and intercept from the standard addition graph were used for further comparison of the matrix modifiers.　The slope of the standard addition graph for the Seta River water compared to that of pure water is very important because it has been regarded as a measure of the chemical interference for the determination of aluminum in the Seta River water.　If the slope ratio was near one, the matrix modifier was effective enough to suppress the chemical interference.

Age of a cuvette.　Before the discussion of the slope ratio, we prepared the table on the age of a cuvette as shown in Table 3.　In the table, the firing times before the experiment were given for 10 independent data points.　It should be noted that not necessarily the same cuvette was used for one matrix modifier, and only one kind of matrix modifier was used for one cuvette.　The age of a cuvette may be shortened with the matrix modifiers containing 1000 ppm palladium, i. e., nos. 2, and 8.　It was possible to use a cuvette

Table 3　The number of firing times of a cuvette

The number of the matrix modifier							
①	②	③	④	⑤	⑥	⑦	⑧
0	0	0	0	10	0	0	0
0	0	24	0	45	0	0	0
102	0	87	43	50	62	46	0
133	42	161	45	86	87	50	0
148	42	161	86	96	151	73	43
195	85	172	142	143	151	145	46
290	87	256	223	200	196	192	93
335	94	352	283	203	258	202	143
402	99	401	375	242	396	247	192
447	290	444	420	336	440	323	273
Mean 205.2	73.9	205.8	161.7	141.4	174.1	127.8	79

The number was sorted for the sake of convenience.

which was used over 400 times with the matrix modifiers, nos. 1, 3, 4, and 6.　It is believed that an aged cuvette produces a decreased absorbance.　However, the negative relationship between the slopes of the standard addition graph for pure water was observed only with the matrix modifiers nos. 4 and 6.　As for the aging of a cuvette, the influence may be ignored on the basis of the discussion of the slope ratio described below.

Slope ratio.　We measured the slope ratio ten times each for the eight matrix modifiers.　In Figure 4, the mean values obtained by the two signal operation modes are shown, together with the standard deviation as the error bar.　No difference in the dispersion was statistically observed between the two signal operation modes.　There was a significant difference in the 95% confidence level between the mean values obtained by the two signal operation modes for the matrix modifiers nos. 1, 3, 4, 5, and 6, i. e., the mean value obtained by the peak–area mode was
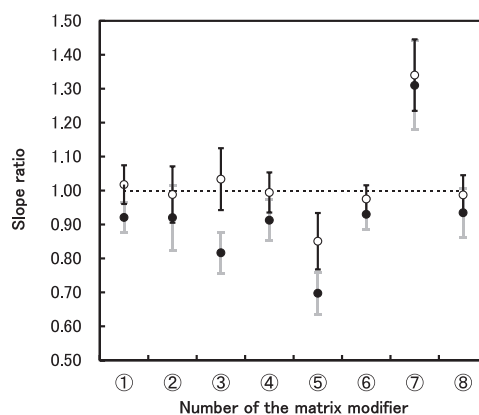

Figure 4　The slope ratio of the standard addition graphs obtained in the two signal operation modes ; the peak–area mode(○) and the peak–height mode(●).　The slope for the Seta River water was divided by the slope for pure water.　The mean value of 10 independent data points is shown in the figure together with its standard deviation.

higher than that obtained by the peak-height mode. Although statistically not significant, the slope ratio obtained by the peak-height mode was lower for the remaining matrix modifiers, nos. 2, 7 and 8.

The chemical interference as evaluated by the slope ratio was influenced by the signal operation mode. In the peak-area mode, the mean value of the slope ratio was near 1.00 for the matrix modifiers, nos. 1, 2, 3, 4, 6 and 8. Irrespective of the signal operation modes, a rather small slope ratio was obtained with the matrix modifier, no. 5, of 100 ppm Mg. In a previous paper[7], we used 1000 ppm Mg as $Mg(NO_3)_2$, i. e., 164 ppm as Mg. At such a low concentration, the effect of the modification was not satisfactory even in the peak-area mode. It is interesting that the effect of the modification increased if nitric acid was included even at the same concentration of magnesium (see nos. 3 and 5).

Obviously, an abnormal result was obtained with the matrix modifier, no. 7, of 100 ppm Pd. The reason why the slope ratio was so high is that the slope obtained with pure water was always very low compared with that of the Seta River water. In the review paper written by H. M. Ortner et al.[36], it was stated that the palladium modifier produced an intercalation compound with graphite. This fact may be the reason for the abnormal result of no. 7, however, it is surprising that the abnormality of the palladium modifier had almost vanished when its concentration was as high as 1000 ppm (see no. 8).

Al concentration in Seta River water. The aluminum concentration in the Seta River water was determined for two signal operation modes and compared with each other. The mean value and its standard deviation of the difference in the determined values for 10 independent data is given in Table 4, together with the paired Student's **t**.[37] The range of the determined values for 80 data points was $0.1 - 0.6 \mu mol \, dm^{-3}$ and its mean value was $0.32 \, \mu mol \, dm^{-3}$. The mean values of the ten determined values (obtained by the peak-area mode) for the matrix modifiers, nos. 1 -8, were 0.333, 0.320, 0.320, 0.345, 0.266, 0.264, 0.361, and $0.360 \, \mu mol \, dm^{-3}$, respectively. It should be noted that the comparison of the mean concentration was impossible because the 10 samples were different for each matrix modifier.

The student's **t** test revealed that five matrix modifiers out of eight showed a difference between the determined values for the two signal operation modes, which was statistically significant at the 95% confidence level. In the matrix modifiers, nos. 1 and 3, the peak-height mode gave larger value than the peak-area mode,

Table 4　Paired Student's **t**-test for the determination of aluminum in the Seta River water using the peak-height mode (PH) and the peak-area mode (PA)

No. of modifier	Difference in the concn. of Al determined by two signal operation modes			
	Mean(n＝10)	Standard deviation	Paired Student's **t**	Result
1	− 0.040	0.032	− 3.93	significant (PH<PA)
2	0.024	0.032	2.36	significant (PH>PA)
3	− 0.031	0.041	− 2.37	significant (PH<PA)
4	0.018	0.018	3.06	significant (PH>PA)
5	− 0.018	0.049	− 1.18	not significant
6	0.028	0.030	2.90	significant (PH>PA)
7	0.020	0.033	1.92	not significant
8	0.007	0.042	0.54	not significant

The critical value (P＝ 0.05, freedom 9) is 2.26.

while for the matrix modifiers, nos. 2, 4, and 6, the peak–area mode gave larger values than the peak–height mode. This difference may be related to the concentration of Mg in the matrix modifier. No such difference was observed in the Pd modifiers at both concentrations (i. e., nos. 7 and 8).

In the 100 ppm Mg modifier, no. 5, the difference was not detected partly due to the high dispersion of the data. However, the tendency was consistent with that using the 164 ppm Mg modifier, as described in a previous paper.[7]

Blank value. Further investigation will be needed to discuss why the difference in the aluminum concentration occurred according to the signal operation modes. In a previous paper,[7] we discussed this problem with respect to the effect of chemical interference to the blank solution. For the measurement of the Seta River water, the peak profile was broader and the peak–height was smaller than that of the standard aluminum solutions due to a chemical interference. Only the blank values had no chemical interference, because we used pure water as the measurement of the blank value even for the Seta River water. Ideally, we have to use the Seta River water in which no aluminum was present for the measurement of the blank value. However, this is not easy to put into practice. If pure water was used for the measurement of the blank value, it is desirable to use a matrix modifier in which the residual concentration of aluminum was as low as possible. The residual concentration of aluminum in the matrix modifier can be estimated from the measurement of the blank value, because the blank value was measured with the mixed solution of $10 \mu L$ of pure water and the aluminum standard solution of concentration zero (i. e., standard zero)

and 5 μL of the matrix modifier. The measurement of the blank solution of this composition was carried out three times (two times for the standard addition measurement for pure water and one time for the Seta River water). The blank values totaled 30 for 10 data points. In Figure 5, the mean value of the blank values is shown together with its standard deviation as an error bar. These data should be regarded to show a slight tendency because the reproducibility of the blank data was rather poor. However, several interesting results can be seen from Fig. 5. First, the blank values were rather high for the (Pd+Mg) and Pd matrix modifiers (nos. 1, 2, 7 and 8). It is natural that these matrix modifiers contain aluminum in relatively high concentrations, because they were originally not intended for the aluminum determination. Second, the blank level of the Mg modifiers (nos. 3, 4, 5 and 6) were higher for nos. 3 and 4 than for 5 and 6. This result means that the effect of the addition of nitric acid was greater than the effect of magnesium
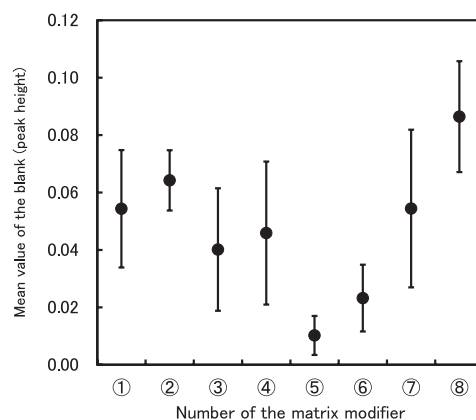

Figure 5 Blank values for each modifier. Blank was measured for the mixture of $10 \mu L$ of the standard 0 (pH was adjusted to ca. 4 by the addition of nitric acid), $10 \mu L$ of pure water and $5 \mu L$ of the matrix modifier. The mean value of 30 independent data points is shown in the figure together with its standard deviation.

concentration on the residual concentration of aluminum. It is quite likely that the contamination of aluminum occurred more significantly if a matrix modifier solution was highly acidic due to the addition of nitric acid. It is very difficult to remove residual aluminum in the original solution of the highly acidic matrix modifier. With respect to the blank, it is desirable to use the matrix modifier, nos. 5 or 6.

Characteristic mass. As a measure of the sensitivity, the concept of the characteristic mass was defined and has been used among the GFAAS researchers.[38] The characteristic mass was defined to be the mass of an analyte which produces an increase in the signal from 0 to 0.0044 units. Therefore, the characteristic mass changes according to the signal operation modes. In our measurement scheme, the characteristic mass can be calculated from the slope of the standard addition graph for pure water. In Figure 6, the mean value of the characteristic mass is shown for the two signal operation modes. Because the slope obtained by the peak–height mode was 2.0 – 2.6 times higher than that by the peak–area mode, the characteristic mass was smaller in the peak–height mode. Among the tested matrix modifiers, the characteristic mass was 4 – 6 pg in the peak–height mode and 8 – 14 pg in the peak–area mode. In comparison with the characteristic mass that appeared in a literature, these values were fairly small, that is, a high sensitivity. For example, Bermejo–Barrera et al. reported the characteristic mass of 26.8 pg (peak–height mode) for the matrix modifier containing the mixture of palladium and magnesium.[18] Ranau et al. reported the characteristic mass of 15 pg (peak–area mode) with the same kind of matrix modifier.[19]
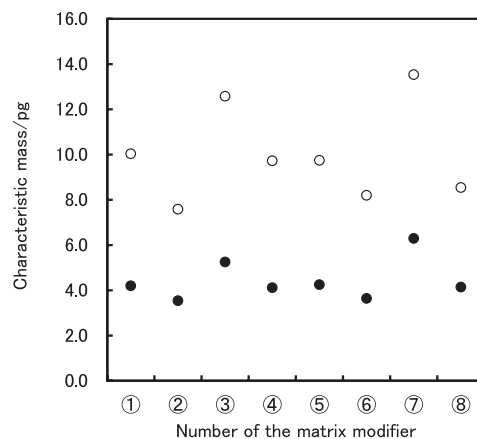

Figure 6　Characteristic mass calculated from the slope of the standard addition graph for pure water. Because the slope obtained from the peak–height mode was about two times higher than that from the peak–area mode, the characteristic mass calculated from the former (m_p) denoted by the closed circle was smaller than that from the latter (m_o) denoted by the open circle.

The characteristic mass obtained with the 100 ppm Pd modifier (no. 7) was the highest among the tested matrix modifiers. Interestingly, the characteristic mass obtained with the other 100 ppm matrix modifiers, nos. 1, 3 and 5, was higher than that obtained with the 1000 ppm matrix modifiers, nos. 2, 4 and 6. This means that 100 ppm was too low as the appropriate concentration for the matrix modifier.

Peak profile. Figure 7 shows the typical examples of the peak profile for the Seta River water and 0.8 μmol dm^{-3} aluminum standard solutions. A small shoulder or a peak distortion during the initial part of the peak profile sometimes appeared as shown by the horizontal arrow. This phenomenon appeared only for the Seta River water with the matrix modifier, nos. 2 and 7, while for the aluminum standard solution with the matrix modifier, nos. 1 and 3, and to both samples with the matrix modifiers, nos. 5 and 8. As a matter of course, such
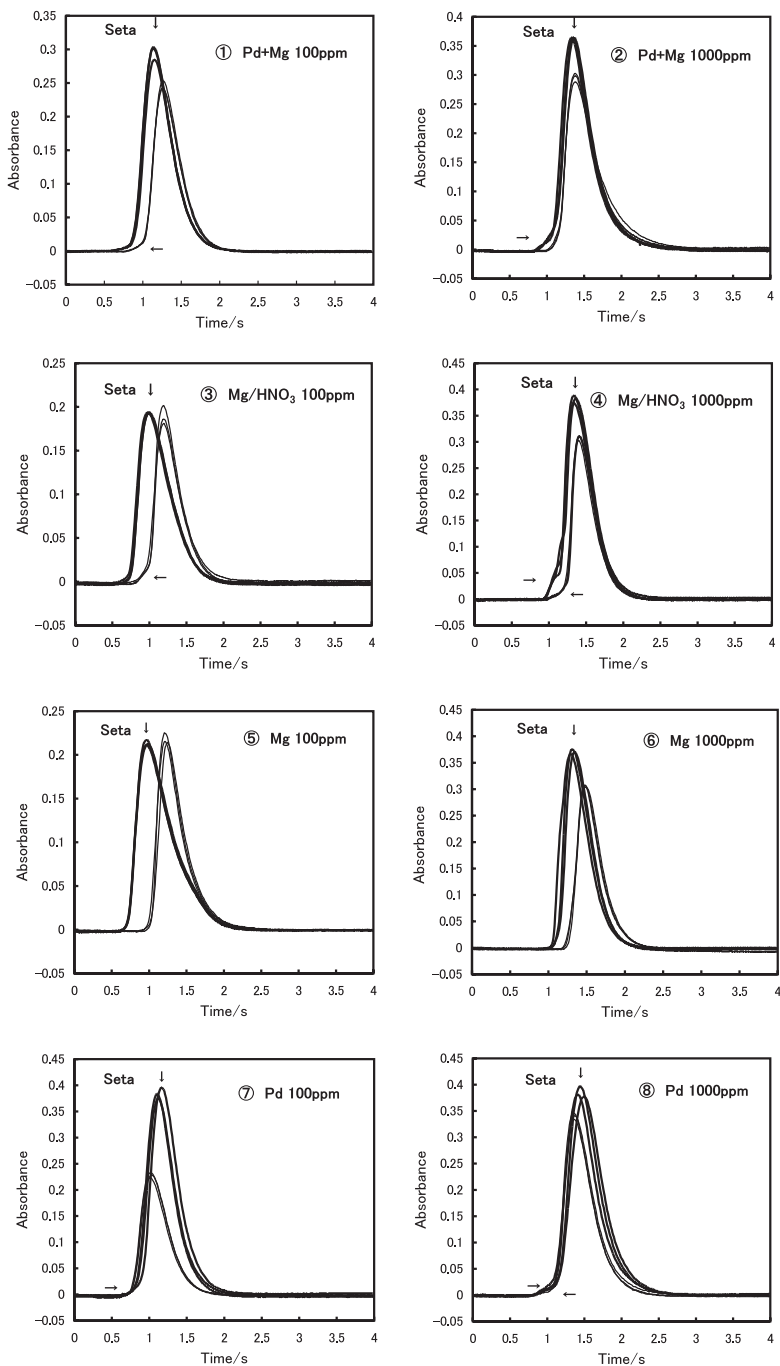
Figure 7   The peak profile recorded by the measurement of the Seta River water (bold lines denoted by a downward arrow) and $0.8\,\mu$mol dm^{-3} aluminum standard solution. The measurements were repeated three times. A small shoulder (or a distortion) appeared in some cases as shown by the horizontal arrow. The left-facing arrow ($\leftarrow$) denotes it for the Seta River water and the right-facing arrow ($\rightarrow$) denotes it for the aluminum standard solution.
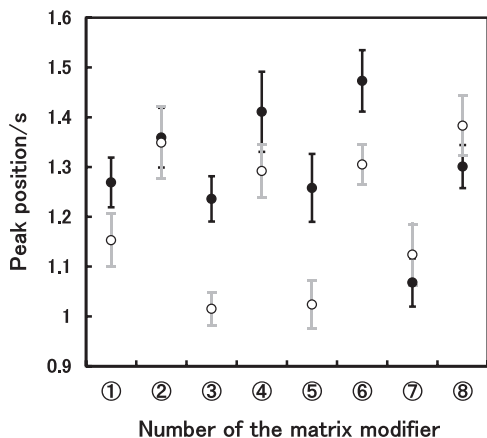
Figure 8   The peak position of the Seta River water(○) and $0.8\,\mu$mol dm^{-3} aluminum standard solution(●). The mean value of 10 independent data points is shown together with its standard deviation.

phenomenon is not desirable for obtaining a correct peak−area. A normal peak profile was always observed with the matrix modifier, nos. 5 and 6. The phenomenon might be related to the nitric acid contained in all the matrix modifiers except for nos. 5 and 6.

As shown in Figure 7, the peak position for the Seta River water and the aluminum standard solution was not always the same for each other. Figure 8 shows the mean value of the peak position with the standard deviation for the Seta River water and $0.8\,\mu$mol dm^{-3} aluminum standard solutions. If the difference in the peak positions for them appeared, it means that there is a difference in the atomization speed. The atomization of aluminum in the Seta River water became faster with the matrix modifiers, nos. 1, 3, 4, 5, and 6, while it was slower with the matrix modifiers, nos. 7 and 8. No difference was observed with the matrix modifier, no. 2, which means that the peak position was not influenced by the co−existing ions in the Seta River water.

The atomization of aluminum was always slower in the more concentrated one of the four sets of matrix modifiers.

Contrary to our expectation, the difference in the peak position for the Seta River water and $0.8\,\mu$mol dm^{-3} aluminum standard solutions was not necessarily in relation to the slope ratio in both signal operation modes. It means that the difference in the peak position for both samples cannot be regarded as a measure of the chemical interference.

Conclusion

The matrix modifiers containing Pd (nos. 1, 2, 7 and 8) was not suitable for the determination of aluminum in the Seta River water, because of their high blank value and/or the abnormal peak profile. Magnesium modifiers containing nitric acid (nos. 3 and 4) were also not suitable for the same reasons. The concentration of magnesium should be as high as 1000 ppm. The electrode used in the device is composed of copper. Nitric acid easily dissolves the copper electrode because of the high operating temperatures. Since no effective measures for this corrosion problem seems to be taken into consideration in the GFAAS, the unnecessary use of nitric acid should be avoided. We concluded that 1000 ppm magnesium nitrate not containing nitric acid may be best among the tested matrix modifiers, although the chemical interference was not fully suppressed. Further research work on the suitability of the 1000 ppm magnesium nitrate matrix modifier for the determination of aluminum is now underway.

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