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Determination of Minor and Trace Metals in Aluminum and Aluminum Alloys by ICP-AES; Evaluation of the Uncertainty and Limit of Quantitation from Interlaboratory Testing

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Minor and trace metals in aluminum and aluminum alloys have been determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) as an interlaboratory testing toward standardization. The trueness of the measured data was successfully investigated to improve the analytical protocols, using certified reference materials of aluminum. Their precision could also be evaluated, feasible to estimate the uncertainties separately. The accuracy (trueness and precision) of the data were finally in good agreement with the certified values and assigned uncertainties. Repeated measurements of aluminum solutions with different concentrations of the analytes revealed the relative standard deviations of the measurements with concentrations, thus enabling their limits of quantitation. They differed separately and also showed slightly higher values with an aluminum matrix than those without one. In addition, the upper limit of the detectable concentration of silicon with simple acid digestion was estimated to be 0.03 % in the mass fraction.

Keywords Aluminum alloy, ICP-AES, accuracy, trueness, precision, uncertainty, limit of quantitation, interlaboratory testing

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Introduction

Aluminum is sufficiently light and strong to be widely used in industry, which has commonly been employed for transport facilities, such as railways, vehicles, aircrafts, vessels, containers, *etc*. Vast kinds of alloys containing magnesium, manganese, copper, silicon, zinc and other elements are prepared, followed by rolling and a heat treatment to enhance their strengths. They are also effective for the architecture as structural materials; moreover, for high-voltage power lines because they can carry twice the current compared to copper alloys based on the same weight condition. In addition, the effects of trace impurities therein have been investigated by specialists in material sciences. Accordingly, the chemical compositions of aluminum and its alloys have already been standardized from minor to trace amounts in ISO (International Organization for Standardization),[1–4] ASTM (American Society for Testing and Materials),[5] and JIS (Japan Industrial Standard),[6,7] in order to maintain their qualities in industry. Trace elements as impurities are also needed to monitor because the chemical composition of an aluminum alloy is one of the factors that determine the final properties of the metal, such as the strength, hardness, and durability. For example, trace amounts of bismuth and boron are known to affect the etching of aluminum electrolytic capacitor foil,[8] and high-purity aluminum more than 5N is needed as a sputtering target for the semiconductor industry to obtain reliable circuits.[9] In the standards of unalloyed aluminum,[1,6] silicon, iron, copper, manganese, magnesium, zinc, titanium, gallium, and vanadium and other elements on high-grade pure metals (ISO and JIS designates “Al 99.995”) are restricted to not contain more than from 0.001 to 0.003 % in each mass fraction as upper tolerable limits of the concentration. ASTM also designates a similar composition as the maximum percentage mass fractions.[5]

However, the standardization of analytical methods to determine trace metals is relatively insufficient. Methods for determination of several trace elements in aluminum materials with photometry and flame atomic absorption spectrometry were separately provided in JIS, and ISO only possesses similar standards with identical methods, but only a part of the JIS series. In contrast, industrial laboratories usually employ analytical methods with ICP-AES, which is nowadays the most conventional *de facto* standard instrumental methods for trace analysis of metals. Although an ICP-AES method for aluminium and aluminium alloys has been standardized as JIS in 1993,[10] and several methods for determination of separate elements have also been designed thereafter,[11–17] the ICP-AES method is highly instrumental, and is prone to be outdated within ten

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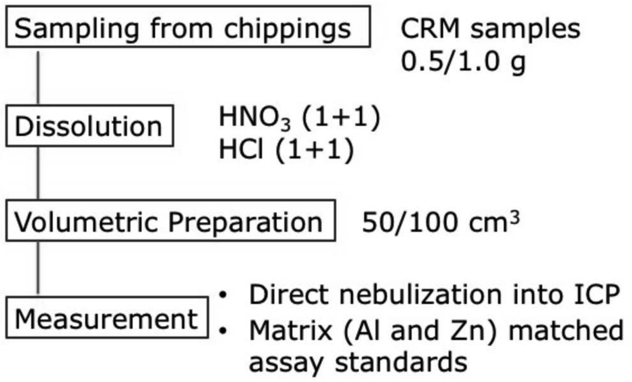

Fig. 1 Analytical protocol for interlaboratory testing.

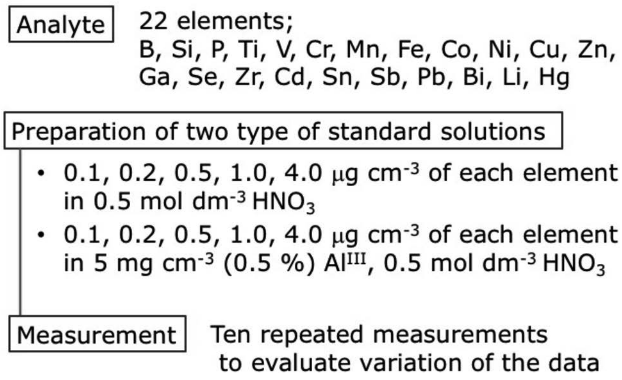

Fig. 2 Analytical protocol for estimating the limit of quantitation.

years, especially concerning to sensitivity and concentration range for determination. ASTM has recently standardized a performance-based ICP-AES method on aluminum and aluminum alloy analysis,[18] it is significant and practical, but is an arranged report come from interlaboratory testing without any evaluation and does not meet requirements from the material standards. Besides, all of the existing analytical standards are not fit for determining designated levels of impure metals in standardized high-pure aluminum as mentioned earlier. It is now time for us to criticize and establish a method for standardization along with an evaluation of the measurement reliability to meet the material standards, which is a consequence of industrial demand.

Moreover, it is an issue to show how the concentration ranges can be rationally designed. Although any analytical standard is requested to denote the applicable concentration range for each element to be analyzed, the way to denote it has still not been settled experimentally. The limit of quantitation (LOQ) is surely a proper index concerning the minimum limit of concentration to be defined, which is strictly differentiated from the limit of detection. Some methods to estimate LOQ were conceptually proposed,[19] yet they have not been applied to real samples with a matrix.

In this study, one aim is to evaluate the method to be standardized. Accuracy of the analytical results both regarding precision and trueness was tested using certified reference materials (CRM). Another aim is to deduce the limit of quantitation (LOQ) from experimental data.

Experimental

CRM samples

Seven aluminum alloys with five classifications were selected to use as CRMs for evaluation. Various aluminum and aluminum alloys are designated as a series of wrought aluminum and aluminum alloys, named as from 1000 to 7000 series in the standard.[3,5,6] The CRMs used were 1000, 4000, 5000, 6000, 7000 series wrought alloys[3] and casting alloys[4] in disk shapes, which were purchased from Alcan Inc. (114/03 and 6063/H1), German Federal Institute for Material Research and Testing (BAM, Berlin) (M312 and M315), and European Commission, Joint Research Centre (Geel, Belgium) named as European Reference Materials (ERM) (EB313, EB316 and EB317).

Interlaboratory testing

A study with respect to standardization of an analytical method requires a specific approach. Once a method is standardized, it should be held in common between all parties concerned.[20] It should satisfy not only chemists, but applied researchers and technicians with various environments and skills. Hence, interlaboratory testing with an analytical protocol is needed to evaluate the method. It must possess some prerequisites: procedure with experienced handling, such as the separation and preconcentration are avoided as much as possible; commercial ICP-AES instruments are almost suitable for measurements in the method; reagents and glassware are commercially available and easily obtainable in laboratories. Moreover, it is desirable to meet routine analysis.

In this study, co-authors, who are experienced technicians in laboratories of Japanese aluminum companies, contributed as participants of the testing. The top author arranged for the CRMs and made the protocol to offer for them.

Analytical protocol

The lastly proposed analytical protocol for interlaboratory testing is shown in Fig. 1. Since a comprehensive description of the protocol may only cause the testing to be more intricate, procedures of simple dissolution with acids and volumetric preparation, sample nebulization, and matrix matched assay standards for calibration were suitable for the test. According to the simple protocol, participants were requested to analyze minor and trace elements in the CRMs with ICP-AES they used in their daily analysis. The CRM samples purchased were chipped with a lathe, packed and sealed by one of the co-authors, then sent to the participants. According to the protocol, they were dissolved with HNO_3 and HCl, and then introduced into ICP-AES with solution nebulization.

Another protocol for estimating LOQ is shown in Fig. 2. A series of assay standard solutions of mixed analyte elements with five different concentrations were prepared from solutions of the commercially available standard or self-prepared standards, the latter of which were made by dissolving highly pure metals. The concentration levels were set to be fairly low enough to evaluate the LOQ, but adequate levels of the concentration were related to the sensitivity of the instruments. The net intensities of the ICP spectra, which were obtained by subtracting a blank intensity from a peak one, were measured repeatedly to evaluate the dispersion of the measured data. Ten repeated measurements were specified in the protocol to calculate the relative standard deviation (RSD), thus enabling one to examine any correlation between the RSD and the concentration. Because LOQ must be defined as the minimum concentration to be determined with the definite RSD,[21] plotting

Table 1 Instruments of ICP-AES used in the interlaboratory testing

Lab. No	Model	Vendor	Viewing position	Nebulizer	Spray chamber	Spectrometer	Detector
1	SPS 3100	Seiko	Radial	Concentric[a]	Cyclonic	Czerny–Turner	PMT
2	ICPS-8100	Shimadzu	Radial	Concentric[a]	Cyclonic	Czerny–Turner	PMT
3	Vista Pro	Varian	Axial	Concentric[a]	Cyclonic	Echelle	CCD[b]
4	CIROS-120	SPECTRO	Axial	Concentric[a]	Cyclonic	Paschen–Runge	CCD[b]
5	ICPS-8100	Shimadzu	Axial	Concentric	Cyclonic	Czerny–Turner	PMT

a. Nebulizers for high salt concentration. b. CCD is a type of semiconductor device named charge coupled device.

Table 2 Average values and calculated uncertainties of elements in 114-3 CRM and their certified values with assigned uncertainties

Element Unit	Si %	Fe %	Cu %	Mn %	Mg %	Cr %	Ni %	Zn %	Ti %	B %	Bi %	Cd %	Co %	Ga %	Li %	P %	Pb %	Sb %	Se %	Sn %	V %
Results																					
Average	0.0031	0.0049	0.0017	0.0019	0.0014	0.0005	0.0009	0.0001	0.0004	0.0088	0.0011	0.0032	0.00103	0.0010	0.0002	0.0004	0.0017	0.0019	0.00019	0.0012	0.00007
Number of data	5	6	6	6	6	6	6	5	6	6	6	6	6	6	5	5	5	5	5	5	5
σ_{n-1}	0.00062	0.00082	0.00028	0.00032	0.00023	8.3×10^{-5}	0.00015	3.3×10^{-5}	7.5×10^{-5}	0.0029	0.0003	0.00067	0.00017	0.00017	0.00004	0.00008	0.00034	0.00038	6.3×10^{-5}	0.0003	1.8×10^{-5}
Uncertainty[a]	0.0003	0.0003	0.0001	0.0001	0.0001	0.0000	0.0001	0.0000	0.0000	0.0012	0.0001	0.0003	0.0001	0.0001	0.0000	0.0000	0.0002	0.0002	0.00003	0.0001	0.00001
Certificate																					
Certified value	0.0034	0.0050	0.0018	0.0019	0.0013	0.0006	0.0009	<0.0002	(0.0004)	0.017	0.0011	0.0031	0.00104	0.0011	0.0002	0.0004	0.0017	0.0021	0.00011	0.0012	0.00008
Uncertainty	0.0004	0.0005	0.0002	0.0002	0.0002	0.0002	0.0002	—	—	0.001	0.0002	0.0002	0.0001	0.0002	0.0001	0.0002	0.0002	0.0003	0.00005	0.0002	0.00004

a. Uncertainty is calculated using the formula $u = \sigma_{n-1}/\sqrt{n}$; σ_{n-1}, standard deviation; n, number of data.

the correlation allows one to estimate the LOQ. Another series of standard solutions with aluminum matrix was also prepared and measured in order to know the matrix effect of aluminum. A solution of high pure aluminum (99.999 % in purity) with a concentration of 10 mg cm^{-3} was prepared in a lump and sent as an aliquot to the participants in order to eliminate any contamination effect in each laboratory.

Results and Discussion

ICP-AES instruments

The participants used several models of ICP-AES instruments in the interlaboratory testing, as listed in Table 1. The instruments had some different characteristics in that the spectrometers were monochromatic (Czeny–Turner type) and polychromatic (Echelle and Paschen–Runge types); also, the viewing positions were radial and axial, and the detectors were photomultiplier (PMT) and charge-coupled devices, one of the charge transfer devices (CTD), all of which were favorable for standardization, considering that the instruments should be available for the method to be standardized.

Accuracy of the interlaboratory testing

The analytical results of minor and trace elements in every CRM sample are comprehensively shown in Tables 2 to 8, in which their certified values with uncertainties are also shown for comparison. Five participants determined from 15 to 23 elements in each CRM sample. The analytical data were simply averaged because they were short enough in numbers to make a statistical test for outliers. Their uncertainties could be calculated using the standard deviations and number of runs, because the averages were good in trueness. The results were totally satisfactory with few exceptions, *i.e.*, most average values showed fairly good agreement with the certified values, and their calculated uncertainties were set within the assigned uncertainties in the certificates. Several remarks concerning the exceptions in the tables are described as follows.

Table 2; The value of boron was averaged, including definitive outliers. That of selenium had large dispersion due to insufficient sensitivity.

Table 3; The value of tin was slightly biased, probably due to the spectral resolution of the instrument because the data obtained with a Czeny–Turner monochromator showed up better.

Table 4; Slightly biased values of lithium and antimony arose from insufficient sensitivity. That of gallium was supposedly due to an over-correction of the spectral interference by chromium. Silicon was too high in concentration to be dissolved with acids.

Table 5; The values concerning bismuth, antimony, and strontium lack in numbers, thus deteriorating their accuracy.

Table 6; The value of copper was slightly biased, probably because the copper concentration in solution seemed to be very high to be determined, thus causing a faintly inferior calibration.

The values of silicon were lower than those of the certificate in Tables 3, 4, and 7. In contrast, they were consistent with each other in Tables 2 and 6. In all cases, the samples were dissolved with nitric and hydrochloric acid, although it is natural to add alkali first in order to increase the solubility of silicon compounds as silicate ion when silicon in aluminum is measured.[11] In this study, simple dissolution with acids was ventured to make sure of the allowable measurable concentration, from a viewpoint of analytical performance. The results revealed that silicon included within *ca.* 0.03 % was practicable to determine using this method.

Therefore, the accuracy of the data from interlaboratory testing, which should be evaluated as trueness and precision, were satisfactory and the proposed method was suitable for standardization.

Estimation of the limit of quantitation

Repeated measurements on the series of standard solutions prepared by degrees allowed us to investigate the relationships between the concentrations and the relative standard deviations (RSD) on the measurements. The relationships were plotted as log-log graphs, thus enabling us to draw lines for easier estimations of LOQ. They could be separately illustrated for each element and each participant. Figure 3 shows an example

Table 3 Average values and calculated uncertainties of elements in 6063H1 CRM and their certified values with assigned uncertainties

Element Unit	Si %	Fe %	Cu %	Mn %	Mg %	Cr %	Ni %	Zn %	Ti %	Cd %	Pb %	Sb %	Sn %	V %	Zr %
Results															
Average	0.474	0.372	0.106	0.166	0.991	0.043	0.052	0.106	0.106	0.00258	0.00308	0.0021	0.0033	0.02042	0.01838
Number of data	3	6	6	6	5	6	6	6	6	6	5	3	6	6	6
σ_{n-1}	0.324	0.012	0.0075	0.010	0.115	0.0015	0.0035	0.0043	0.0037	0.00017	0.00069	0.0016	0.0005	0.0014	0.0013
Uncertainty[a]	0.188	0.005	0.003	0.004	0.051	0.001	0.001	0.002	0.001	0.0001	0.0003	0.001	0.0002	0.0006	0.0005
Certificate															
Certified value	0.64	0.360	0.105	0.159	0.93	0.041	0.052	0.105	0.105	0.0026	0.0033	—	0.0027	0.0205	0.0194
Uncertainty	0.02	0.015	0.005	0.005	0.04	0.002	0.002	0.005	0.005	0.0002	0.0003	—	0.0003	0.0010	0.0020

a. Uncertainty is calculated using the formula $u = \sigma_{n-1}/\sqrt{n}$; σ_{n-1}, standard deviation; n, number of data.

Table 4 Average values and calculated uncertainties of elements in EB-313 CRM and their certified values with assigned uncertainties

Element Unit	Si %	Fe %	Cu %	Mn %	Mg %	Cr %	Ni %	Zn %	Ti %	B ppm	Bi ppm	Cd ppm	Co ppm	Ga ppm	L ppm	P ppm	Pb ppm	Sb ppm	Sn ppm	V ppm	Zr ppm
Results																					
Average	0.329	0.385	0.094	0.494	3.347	0.1221	0.0266	0.156	0.0969	7.1	90	7.1	8.4	113	5.7		43.1	25.8	187	296	366
Number of data	2	6	6	6	6	6	6	6	6	3	5	6	5	6	6		5	3	6	6	6
σ_{n-1}	0.045	0.009	0.006	0.015	0.123	0.008	0.0005	0.004	0.0075	7.1	3.0	0.3	0.6	4.8	0.4	—	5.8	20.6	13.0	6.9	34.7
Uncertainty[a]	0.032	0.0037	0.0026	0.0061	0.050	0.0033	0.0002	0.002	0.0031	3.5	1.5	0.1	0.3	1.9	0.2	—	2.6	11.9	5.3	2.8	14
Certificate																					
Certified value	0.363	0.391	0.0931	0.495	3.40	0.1224	0.0278	0.158	0.0947	5.0	95	7.4	—	121	6.04	12.9	43.3	8.7	197	299	359
Uncertainty	0.007	0.003	0.0014	0.003	0.04	0.0012	0.0006	0.002	0.0014	—	8	0.4	—	5	0.12	—	2.8	1.9	6	6	19

a. Uncertainty is calculated using the formula $u = \sigma_{n-1}/\sqrt{n}$; σ_{n-1}, standard deviation; n, number of data.

Table 5 Average values and calculated uncertainties of elements in EB-316 CRM and their certified values with assigned uncertainties

Element Unit	Fe %	Cu %	Mn %	Mg %	Ni %	Zn %	Ti %	Cr ppm	B ppm	Bi ppm	Cd ppm	Co ppm	Ga ppm	Li ppm	Pb ppm	Sb ppm	Se ppm	Sn ppm	V ppm	Zr ppm	Sr ppm
Results																					
Average	0.1060	0.0291	0.204	0.0458	0.0229	0.0612	0.0785	60.5	1.8	125	20.6	1.4	97	0.9	83	43	0.7	106	97	32.8	265
Number of data	6	6	6	6	6	6	6	6	1	4	6	2	6	2	5	3	1	6	6	6	1
σ_{n-1}	0.0028	0.0011	0.0035	0.0007	0.0014	0.0021	0.0014	4.2	—	17.8	1.2	0.46	9.2	0.47	8.3	18	—	6.6	6.5	3.8	—
Uncertainty[a]	0.0012	0.0005	0.001	0.0003	0.0006	0.0008	0.0006	1.9	—	9	0.5	0.3	3.8	0.3	4	13	—	3	3	1.6	—
Certificate																					
Certified value	0.1054	0.0297	0.204	0.045	0.0235	0.0611	0.079	59.3	<1.5	140	20.8	<1.5	105	1	87	56	—	106	98	32.8	206
Uncertainty	0.0021	0.0008	0.004	0.004	0.0011	0.0012	0.0015	2.6	—	7	1.5	—	5	—	7	5	—	11	7	0.7	7

a. Uncertainty is calculated using the formula $u = \sigma_{n-1}/\sqrt{n}$; σ_{n-1}, standard deviation; n, number of data.

Table 6 Average values and calculated uncertainties of elements in EB-317 CRM and their certified values with assigned uncertainties

Element Unit	Si ppm	Fe %	Mn ppm	Cu %	Mg %	Zn %	Cr +1%	Zr %	Ni ppm	Ti ppm	B ppm	Bi ppm	Cd ppm	Co ppm	Ga ppm	P ppm	Pb ppm	Sn ppm	V ppm	In ppm
Results																				
Average	266	0.111	914	1.77	2.49	6.93	0.142	0.134	350	1067	51	33	8	2	167	—	49	225	103	159
Number of data	2	6	6	6	6	6	6	6	6	6	3	5	5	5	6	—	5	6	6	4
σ_{n-1}	13.4	0.002	15	0.040	0.099	0.115	0.010	0.009	10.0	69	2.5	14.2	0.4	0.88	4.0	—	6.6	11	4.1	8.6
Uncertainty[a]	9.5	0.001	6.0	0.016	0.041	0.047	0.0041	0.0	4.1	28.3	1.5	6.4	0.2	0.4	1.6	—	3.0	4.5	1.7	4.3
Certificate																				
Certified value	271	0.112	912	1.77	2.39	6.92	0	0.130	359	952	37	41	—	—	183	27	47.9	237	105	162
Uncertainty	27	0.007	10	0.02	0.16	0.35	0	0.005	12	156	31	11	—	—	18	14	2.0	27	4	34

a. Uncertainty is calculated using the formula $u = \sigma_{n-1}/\sqrt{n}$; σ_{n-1}, standard deviation; n, number of data.

of antimony obtained from the data of one of the participants with concentrations of 0.02 – 4.0 μg cm^{-3}, where the RSD is inversely proportional to the concentration. The lower the concentration becomes, the more the RSD increases, so the relation should be conceptually inversely proportional. If the instrument is sensitive enough to gain sufficient intensities with relatively little RSD, even at the lowest concentration level, a weak relationship would occur in the plot. Hence, some participants decided to prepare solutions of lower concentrations than those in the protocol designated, from 0.0002 to 0.01 μg cm^{-3} for a further investigation. In addition, some of them prepared a series of eight or ten different concentrations for detailed inspections. However, several figures revealed that they could find neither a correlation nor a proportional relation,

Table 7 Average values and calculated uncertainties of elements in M312 CRM and their certified values with assigned uncertainties

Element Unit	Si %	Fe %	Cu %	Mn %	Mg %	Cr %	Ni %	Zn %	Ti %	Bi ppm	Cd ppm	Ga ppm	Pb ppm	V ppm	Zr ppm
Results															
Average	0.144	0.191	0.0433	0.0418	0.423	0.0284	0.00470	0.0288	0.0288	21	24	114	42.6	62	10
Number of data	2	6	6	6	5	6	6	6	6	6	6	4	5	6	6
σ_{n-1}	0.101	0.0049	0.0017	0.0018	0.019	0.0005	0.0003	0.0012	0.0002	4	1	7	2	4	2
Uncertainty[a]	0.071	0.002	0.0007	0.0007	0.009	0.0002	0.00013	0.0005	0.0001	1.6	0.4	4	0.9	1.6	0.8
Certificate															
Certified value	0.415	0.185	0.0419	0.0416	0.409	0.0276	0.00452	0.0290	0.0288	23	22.6	115	43.9	61.5	10.1
Uncertainty	0.006	0.004	0.0008	0.0008	0.005	0.0008	0.00015	0.0004	0.0004	4	1.0	4	2.5	2.3	0.5

a. Uncertainty is calculated using the formula $u = \sigma_{n-1}/\sqrt{n}$; σ_{n-1}, standard deviation; n, number of data.

Table 8 Average values and calculated uncertainties of elements in M315 CRM and their certified values with assigned uncertainties

Element Unit	Si[b] %	Fe %	Cu %	Mn %	Mg %	Cr %	Ni %	Zn %	Ti %	Pb %	Sn ppm	B ppm	Bi ppm	Cd ppm	Co ppm	Ga ppm	Li ppm	P ppm	Sb ppm	Se ppm	V ppm	Zr ppm	Sr ppm
Results																							
Average	9.08	0.59	2.47	0.318	0.426	0.0311	0.096	0.76	0.148	0.074	0.075	21	71	10	3	99	2	45	22	2	53	31	69
Number of data	1	6	6	6	6	6	6	6	6	5	6	1	1	6	2	6	3	2	3	1	6	6	1
σ_{n-1}	—	0.02	0.04	0.01	0.01	0.00	0.01	0.02	0.01	0.03	0.003	—	—	1.3	1.6	8.6	1.1	31.1	13.4	—	4.6	0.90	—
Uncertainty[a]	—	0.010	0.014	0.004	0.0054	0.0011	0.003	0.010	0.003	0.014	0.001	—	—	1	1	4	1	13	8	—	1.9	0.4	—
Certificate																							
Certified value	9.18	0.59	2.51	0.314	0.422	0.0311	0.096	0.77	0.143	0.079	0.0771	<3	41	11	<3	101	—	13	32	—	54	30	69
Uncertainty	0.21	0.02	0.09	0.007	0.012	0.0007	0.003	0.02	0.005	0.004	0.0025	—	7	4	—	5	—	7	24	—	2.5	7	3.9

a. Uncertainty is calculated using the formula $u = \sigma_{n-1}/\sqrt{n}$; σ_{n-1}, standard deviation; n, number of data. b. Silicon is determined with alkali dissolution.

which seems to be due to the high sensitivity, spectral interferences, or contamination, *etc*. Alkali earth metal elements match a typical case, having no correlation. The figures used to estimate LOQs were enormous in amounts, which were consequently compiled as the Supporting Information shown from Figs. S1 to S22, from which Fig. 3 was selected as a typical case, showing clear inverse proportions suitable for estimations. In the figure, when a horizontal line passing the vertical axis of a definite RSD is drawn to cross the correlation line, it is bent to a right angle to draw further till the horizontal intercept, *i.e.* a concentration which means LOD in the RSD denoted. The LOQ linked with RSD could be accordingly estimated using these lines separately. Table 9 gives a list of maximum assessable LOQs from the laboratories, with and without aluminum matrix at 5 and 10 % of RSD. The lower applicable ranges presently stated in the corresponding JIS are added for comparison. All of the LOQs obtained in this study were incomparably smaller than the lower limits of the concentration in the JIS, probably because of the progress concerning the instruments, especially sample introduction units, assisted introduction of a high matrix sample solution with enhanced and stabilized signal intensity. The LOQs with 0.5 % aluminum matrix seem to be larger than those without the matrix. They should be principally larger at RSD 5 % than those at RSD 10 %. However, as a whole, the trend may also have a little more variations by other factors. This study will start a detailed investigation for estimating the determinable concentration limit for real samples with matrixes.

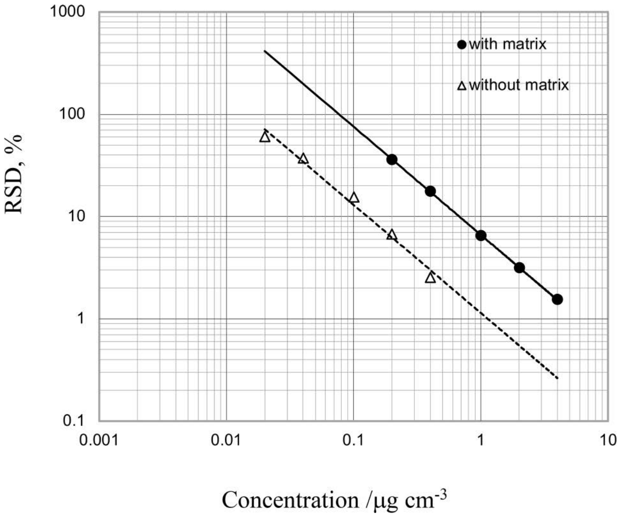

Fig. 3 Log-log plot to estimate LOQ in the determination of antimony.

Conclusions

The interlaboratory testing for determining minor and trace metals in aluminum and aluminum alloys with ICP-AES was totally successful. Five participants submitted accurate analytical results of 15 – 23 elements in seven CRMs of aluminum materials. The analytical method proposed as a protocol is simple and easy to trace with both trueness and precision, which seems to be quite suitable for the standardization of analytical methods. The applicable lowest concentrations of 22 elements, which are indispensable information for constructing analytical standards with instruments, could be rationally estimated by repeated measurements of low concentrations of metals in an aluminum matrix, followed by a log-log plot. The established method will be proposed as a new

Table 9 Estimated limits of quantitation at RSD is 5 and 10 % and applicable lower limits taken from corresponding JIS for comparison (unit: μg g^{-1})

Element	RSD 5 %		RSD 10 %		JIS lower limit	Reference No.
	Without matrix	With matrix	Without matrix	With matrix		
B	0.8	0.4			100	14
Si	12	5.4	6.8	3.4	100	11
P	16	18	7	10	—	
Ti	0.14	0.2	0.08	0.08	20	10
V	0.6	0.5	0.4	0.4	20	10
Cr	0.4	2.2	0.28	0.2	20	10
Mn	0.06	0.6	0.02	0.24	20	10
Fe	0.4	0.4	0.14	0.14	20	10
Co	0.7	0.54	0.36	0.26	—	
Ni	0.8	0.8	0.4	0.5	—	
Cu	1.2	1	0.8	0.5	20	10
Zn	0.18	0.9	0.08	0.5	20	10
Ga	2.6	4	1.6	1.8	—	
Se	5	22	3	13	—	
Zr	0.5	0.5	0.2	0.2	100	12
Cd	0.22	0.84	0.12	0.36	10	17
Sn	2	6	0.84	3	—	
Sb	5	26	2.6	14	—	
Pb	3.4	36	9	26	100	15
Bi	16	20	8	10	100	13
Li	1.6	1.6	0.8	0.8	—	
Hg	4	6	2	4	—	

work item at the ISO technical committee and superseded to update JIS H1307.

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Supporting Information

Log-log graphs of all the elements by every participant. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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