Instrumental Chemical Analysis of Magnesium and Magnesium Alloys

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1. Introduction

Magnesium is the lightest of all the commonly used metals. It is one of the most abundant elements in the earth's surface, amounting to a mass fraction of *c.a.* 2.5 %. It has been prepared for industry as metal and alloy ingots; the latter are most often made with aluminum. Various magnesium-based alloys have been developed and mainly applied to transport facilities and mobile electric devices because they have the best strength-to-weight ratio of any of the commonly used structural alloys. Practically, they are used for housing of laptop computers, mobile phones, and digital cameras, moreover, materials for acoustic diaphragm, units of vehicles, nursing-care equipments, anode for sacrificial protection, *etc*. Some special alloys with rare earth metals, which show high strength properties at elevated temperatures (Rokhlin, 2003), have been recently applied to aircraft and space machinery, automobile and railcar products. Accordingly, the chemical composition of magnesium and its alloys have already been standardized from major to trace quantities. International Organization for Standardization (ISO 8287, 2000; ISO 16220, 2005), American Society for Testing and Materials (ASTM B92/B92M-07, 2007; ASTM B93/B93M-07, 2007), and Japan Industrial Standard (JIS H2150, 2006; JIS H2221, 2006; JIS H2222, 2006) provide the standards of metal ingots, wrought alloys, and casting alloys separately, where vast kinds of designation, chemical constituents with permissible ranges, and chemical impurity with maximal allowable limits are denoted therein. Moreover, the wrought alloys with extruded or forged shapes to make sheets, bars, pipes, tubes, wires, *etc* have been specialized in ISO (ISO 3116, 2007), ASTM (ASTM B107/B107-07, 2007), and JIS as several particular standards. Table 1 shows the chemical composition of unalloyed magnesium with different purities denoted in ISO 8287.

However, standardization of analytical methods to determine metal elements therein is quite insufficient. In 2006, ISO confirmed five old standards for minor analyses with gravimetry and titrimetry, and eleven ones for trace analyses with photometry and atomic absorption spectrometry, all of which were established in the 1970s and 1981. On the contrary, in 2008 ASTM withdrew the standard test methods for chemical analysis in view of a lack of information on reliability therein (ASTM E35-88, 2002), where a chill cast specimen can only be affordable to be analyzed with the ASTM test method using spark source atomic emission spectrometry (ASTM B95435-07, 2007). JIS denotes most plentiful standard methods that feature classical wet techniques and instrumental analyses corresponding with concentrations in the materials and accuracy needed, but they are standardized mostly in 1990's with flame atomic absorption spectrometry for trace analyses. Consequently in all cases, there existed no methods for the determination of trace amounts

of metals with inductively coupled plasma atomic emission spectrometry (ICP-AES), which is nowadays one of the most conventional *de facto* standard instrumental methods for the trace analysis of metal elements. Table 2 shows a list of the analytical methods made up from ISO and JIS standards. In this Table, some new standards of JIS by the author and his members using ICP-AES are also shown in the last four lines, details of which are described below.

Material designation		Chemical composition % mass fraction													
In accordance with ISO 2092	In accordance with EN 12421	min. or max.	Al	Mn	Si	Fe	Cu	Ni	Pb	Sn	Na	Ca	Zn	Others (each)	Mg[a]
ISO Mg 99.5	EN-MB 10010	min. or	-	-	-	-	-	-	-	-	-	-	-	-	99.5
		max.	0.1	0.1	0.1	0.1	0.1	0.01	-	-	0.01	0.01	-	0.05	-
ISO Mg 99.80A	EN-MB 10020	min. or	-	-	-	-	-	-	-	-	-	-	-	-	99.80
		max.	0.05	0.05	0.05	0.05	0.02	0.001	0.01	0.01	0.003	0.003	0.05	0.05	-
ISO Mg 99.80B	EN-MB 10021	min. or	-	-	-	-	-	-	-	-	-	-	-	-	99.80
		max.	0.05	0.05	0.05	0.05	0.02	0.002	0.01	0.01	-	-	0.05	0.05	-
ISO Mg 99.95A	EN-MB 10030	min. or	-	-	-	-	-	-	-	-	-	-	-	-	99.95
		max.	0.01	0.006	0.006	0.003	0.005	0.001	0.005	0.005	0.003	0.003	0.005	0.005	-
ISO Mg 99.95B	EN-MB 10031	min. or	-	-	-	-	-	-	-	-	-	-	-	-	99.95
		max.	0.01	0.01	0.01	0.005	0.005	0.001	0.005	0.005	-	-	0.01	0.005	-
[a] By difference															

Table 1. Chemical composition of unalloyed magnesium denoted in ISO 8287

This chapter outlines instrumental methods of the analysis and especially focuses on ICP-AES. The methods of trace analyses in magnesium and its alloys by ICP-AES are described with results of interlaboratory testing of the analyses, which have been put into practice prior to standardization by the author. The concept of the testing protocol, which must be acceptable for practical technicians with various environments and skills, will be emphasized in the chapter. The protocols evaluated in the testing have been provided as recently established JIS standards, which are the first standardized analytical methods on magnesium and its alloys by ICP-AES.

2. Instrumental methods of analysis

2.1 Outline of the instruments for material analysis

In material analysis, verification and evaluation of chemical components and impure elements mostly designated in standards are indispensable. Hence elemental quantification is first needed with high reliability, which allows atomic spectroscopy to rank first for this kind of analysis.

Atomic spectroscopy has undoubtedly become a major tool on trace analysis of metals in materials, where inductively coupled plasma atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS) have been widely used as archetypal methods around laboratories. They observe atomic spectra on measurement, which are generated in ultraviolet and visible region due to radiative transitions of outer orbital electrons between the ground state and excited state of an atom. The spectra are elementally specific and their signal intensities relate to the concentrations of the elements, thus allowing selective qualification and quantification. Samples must be dissolved with acids to prepare as solutions prior to determination. When the sample solutions are introduced into the instruments, they are made to aerosols with nebulizers, subsequently desolvated and dissociated to atoms with heat sources such as plasmas and flames. In general, obtainable spectra in the atomic spectroscopy can be classified into three categories: (a) spontaneous

emission from a higher excited state to a lower state; (b) absorption of radiation corresponding with a transition from a lower state to a higher state; and (c) induced resonant emission for the transition from a higher state to a lower state just after the absorption of external distinctive radiation. ICP-AES utilizes the spectra of type (a), because high temperature of 5000-6000 K generated in argon ICP makes almost all the atoms in a higher excited state. On the other hand, AAS does the ones of type (b) because kinds of flames generated with acetylene premixed with air or nitrous oxide and electrical furnaces, which are typically suitable as excitation sources for AAS, can reach relatively low temperature in the region of 2000-3000 K only to make them in a lower state. The last category of type (c) is applied to atomic fluorescence spectrometry, which is neither less popular in practical laboratories nor commercially available than ICP-AES and AAS.

element	ISO			JIS		
	method	number:year	dynamic range (%)	method	number:year	dynamic range (%)
Al	gravimerty	791:1973	1.5-12.0	gravimetry	H1332:1999	1.5-12.0
	colorimetry	3255:1974	0.01-0.20	titrimetry	H1332:1999	2.0-11.0
				colorimetry	H1332:1999	0.01-0.20
				flame AAS	H1332:1999	0.0005-0.05, 0.001-0.05
Zn	titrimetry	1783:1973	0.10-8.0	titrimetry	H1333:1999	0.1-7.0, 0.4-7.0
	flame AAS	4194:1981	0.1-6	flame AAS	H1333:1999	0.0002-8.0, 0.1-6.0
Mn	colorimetry	809:1973	0.01-0.8	colorimetry	H1334:1999	0.02-1.0, 0.01-0.8, 0.0002-0.1
	colorimetry	810:1973	<0.01	flame AAS	H1334:1999	0.0005-0.5
	colorimetry	2353:1973	0.02-0.2 *			
Si	colorimetry	1975:1973	0.01-0.6	colorimetry	H1335:1998	0.02-0.50, 0.001-0.05, 0.01-0.6
Cu	colorimetry	794:1976	0.002-0.4	colorimetry	H1336:1999	0.0005-0.5, 0.002-0.4, 0.0003-0.03
				flame AAS	H1336:1999	0.005-0.4
Ni	colorimetry	4058:1977	0.0005-0.05	flame AAS	H1337:1999	0.0002-0.04
Fe	colorimetry	792:1973	0.002-0.05	colorimetry	H1338:1999	0.002-0.05, 0.0005-0.05
				flame AAS		0.001-0.08
Zr(soluble)	colorimetry	1178:1976	0.1-1.0	colorimetry	H1340:1998	0.05-1.0
Zr(insoluble)	colorimetry	2354:1976	0.02-0.3	colorimetry	H1340:1998	0.02-0.3
Th	gravimetry	5196-1:1980	0.2-5.0	-	-	
	titrimetry	5196-2:1980	0.2-5.0			
Rare Earths	gravimetry	2355:1972	0.2-10	gravimetry	H1345:1998	0.2-10.0
Ca	-	-		flame AAS	H1341:1990	0.01-0.1
Sn	-	-		ICP-AES	H1342:2008	0.0005-0.01
Pb	-	-		ICP-AES	H1343:2008	0.0005-0.01
Cd	-	-		ICP-AES	H1344:2010	0.00005-0.001
Be	-	-		ICP-AES	H1339:2010	0.00005-0.001, 0.00005-0.002
				flame AAS	H1339:2010	>0.001

* the method for alloys containing Zr, rare earths, Th, & Ag

Table 2. List of standardized analytical methods for magnesium and magnesium alloys in ISO and JIS

Transitions of electrons take place not only between the outer shells but also from the outer to an inner as a result of external excitation. When X-ray or one of the related beams such as accelerated electron and heavy charged particle (proton or α-particle in usual) is irradiated to an atom, an electron in the inner may be ejected to have a vacancy, producing an excited ion. An electron from the outer shell almost immediately fills it, emitting elementally specific X-ray corresponding to a difference of the two energy levels. This refers to as one of X-ray spectroscopy. Instrumentation with electrically operated X-ray tubes is most conventional and sophisticated as X-ray fluorescence spectrometry(XRF). It needs no dissolution as pretreatment step and allows direct measurements on materials.

Atoms generated in the ICP are easy to lose electrons to become positively charged ions owing to its high temperature, which are feasible to be detected with mass analyzers. Actually major part of elements in the plasma is not atomic but ionic, where the emissions from the transitions in the atoms and ions are both utilized in ICP-AES. Consequently inductively coupled plasma mass spectrometry (ICP-MS) has been developed, combining the ICP and mass analyzers for ultra trace analysis of metals.

Further explanation on the outline should be directed to recently published books on atomic and X-ray spectroscopy including ICP-MS. (Broekaert, 2005; Welz & Borges, 2009) Another book on ICP-AES and ICP-MS is also convenient for Japanese users. (Uemoto, 2008)

2.2 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Atomic emission spectrometry (AES) is the oldest atomic spectrometric technique capable of multi-elemental detection. Chemical flames and plasmas generated on arc, spark, and glow discharges have been used as excitation sources. However, appearance of high frequency plasma has transformed this technique into the cutting-edge one, which is capable of determining trace metals selectively below ppm levels over larger dynamic ranges than any other spectrometric technique. This method is often called as inductively coupled plasma optical emission spectrometry (ICP-OES). The plasma, an ionized gas of argon at very high temperature (5000-6000K), is generated at high frequency (usually 27 or 40 MHz) under argon gas flow in three concentric quartz tubes known as a plasma torch. The torch is encircled at the top by an induction coil connected to a generator, where the magnetic field induced in the gas stream forms the plasma. Its concentrically toroidal structure allows sample solution as an aerosol into the center of the plasma, thus enabling its efficient desolvation, vaporization, atomization, excitation, and ionization. These characteristics of the argon ICP applicable to a wide variety of elements lead to sensitive multi-elemental determination relatively independent of matrix elements. Figure 1 shows a schematic view of the inductively coupled plasma.

ICP-AES consists of simple units as shown in Figure 2. The electromagnetic energy necessary to sustain the plasma is transferred from the high frequency generator unit to the emission unit that consists of the torch and the induction coil. Sample aerosols are carried with argon gas into the plasma, where the emission lights from the plasma are introduced into the spectrometer unit and intensities of monochromated lines are measured in the detector unit, a whole of which is fully regulated by the controller unit.

Device technology in ICP-AES has further been designed and now the instruments have some selectable specifications in relation to the adaptability and performance of the system. The principal innovations to be mentioned are described as follows; Although the ICP can be originally viewed radially (side-on), an alignment for axial (end-on) viewing with horizontally generated plasma has been devised in order to gain sensitivity due to longer path length than the radial viewing. In the former, the plasma is positioned at a 90 deg angle
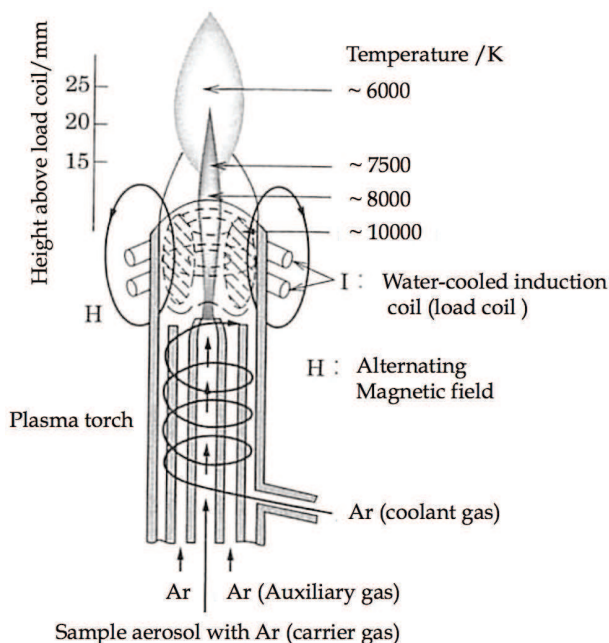
Fig. 1. Schematic view of the inductively coupled plasma

with the detector, while in the latter, the ICP and detector are positioned in the same optical axis. The latter certainly brings higher sensitivity but interferences due to coexisting elements are known to be severe; the spectrometer could be originally divided into two categories; monochromator and polychromator. The former is used to build up sequential scanning system, while the latter is for simultaneous detection system with one detector by one element, both of which utilize the first-order light despersion. Another spectrometer with so-called 'echelle' grating and a prism to spread all the dispersed lights with high orders on a plane has been developed. It seems preferable to set up this spectrometer with the axial viewing system because emission lights dispersed by wavelength with the echelle spectrometer is darker than those with other spectrometers. Detectors to convert lights to electrical currents have greatly been developed. Photomultiplier tube (PMT), consists of a photocathode and a dynode, had been an unique device for receiving photons, efficient amplification of electrons, and generating electrical currents on measurement. Solid-state detectors, all of which are categorized under the term charge transfer device (CTD), are modern types of detectors having state-of-the-art technology. As the PMT is restricted to assess the signal at only one point, it costs not a few time to scan over spectral vicinity around an analyte line. Recent CTDs have several tens of squared micrometers in size, so are feasible to be spread over the area of a focal plane to obtain a two-dimensional picture of the spectra at once. They are called as array detectors and the smallest pictorial unit of a solid-state detector is called pixel. The CTDs are subcategorized in proportion to its characteristics; photodiode array (PDA), charge injection device (CID), charge coupled device (CCD), and segmented charge coupled device (SCCD), where the PDA were only installed in research instruments before development of the other ones. Their selection and usage is up to the vendors of ICP-AES in accordance with their developments.
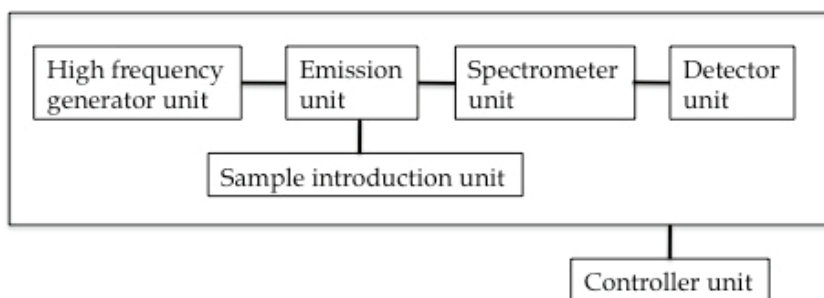
Fig. 2. Components of ICP-AES

In material analysis, a type of the radial viewing is recommended because effects of matrix elements with the radial viewing (magnesium and other minor elements in this case) are lighter than those with the axial one. Another reason can be claimed that damage of the outer tube in the torch during measurement is more severe when plasma turns on horizontally, which is the normal position of the axial viewing geometry.

A practical guide that links with theory and applications has been available to all levels of users (Nölte, 2003).

2.3 Atomic Absorption Spectrometry (AAS)

Another conventional method for determination of trace metals in materials is surely atomic absorption spectrometry. Chemical flames made from acetylene premixed with air or nitrous oxide is typically used for atomization. Electrical furnaces are also used, but all of them have maximum temperatures of c.a. 3000 K as the thermal sources, which cannot allow sufficient atomization for all elements. In addition, matrix interferences are more severe compared to ICP-AES due to relatively low temperatures. Sample solutions are usually aspirated and introduced as aerosols into a laminar flame, through which the specific light beam of an element passes to be absorbed by the atoms. Different from atomic emission, External radiation source is needed for atomic absorption. A hollow-cathode lamp (HCL) is widely used for an intense line source of individual element, which is a glass container with a hollow cylinder as cathode and a ring as anode filled in an inert gas under low pressure. The metal atoms sputtered with the inert gas are excited by collisions with electrons and emit the characteristic atomic emission lines. The bandwidth of the line from HCL is narrow enough that a spectrometer with higher resolution is not required than that of ICP-AES. Another invention in AAS is the modulation system of signal amplification. In all cases, voltage is applied to HCL in an alternating or a pulsing mode, thus emitting intermittent radiation. A detected absorption signal is magnified with a lock-in (phase-sensitive) amplifier that detect signal based on modulation at the same frequency as that of the line source. Consequently AAS can be equipped in relatively low costs and allows easier operation than other techniques on atomic spectrometry. A disadvantage of the AAS is of course on the requirement of setting of single elemental HCL one by one, although continuum source AAS with high resolution optics has recently been appeared on the market. Another disadvantage is the non-linearity of calibration curves due to self-absorption when absorbance becomes higher than 0.5 to 1, where a dynamic range more than one order of magnitude should not be expected.

AAS has a few more techniques on atomization and background correction; they should be referred to a tutorial and technical textbook for further understanding of the characteristics and practices of the AAS. (Vandescasteele & Block, 1993).

2.4 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS is definitely one of the prior tools for ultra trace analysis of metals in materials although sensitive types of modern ICP-AES can afford to measure the metals to a level of ng cm^{-3} (ppb) or so. For example, unalloyed magnesium with high purities must contain less than 0.001 % of lead and 0.00005 % of cadmium as denoted in the ASTM standard, hence measurements to a level of ppb or below in sample solutions are necessarily required for proper evaluation. ICP-MS will surely play a more important role on ultra trace analysis. Several types of mass spectrometers to combine ICP, which are not only quadrupole spectrometer but also magnetic sector, time of flight, ion trap ones *etc*, have been developed. Among ICP-MS equipments those with quadrupole mass analyzer are most popular and often called ICP-QMS. One drawback of ICP-MS in material analysis is that it is not an optical analysis but a particle one, *i.e.* matrix elements introduced to the instrument are stored and accumulated on the mass analyzers and detectors different from the cases of ICP-AES. In ICP-AES, contamination of the matrix elements is restricted to the sample introduction unit that is demountable and easy to clean out. Consequently in ICP-MS, the background levels of matrix elements that appear in a historical record of measurements surely increase gradually due to contamination, which must be unavoidable especially in material analysis. At last, ratios of the concentration of an analyte to the tolerable concentrations of matrix elements to be loaded in the instruments are critical for measurements, not absolute concentration of the analyte. ICP-MS is remarkably more sensitive in the measurements but tolerable maximal concentration is also lower than ICP-AES. Modern technology may reveal that currently equipped ICP-AES should have priority even in the ultra trace analysis of materials.

A comprehensive handbook specialized on ICP-MS should be noticed. (Nelms, 2005)

2.5 Spark source Atomic (optical) Emission Spectrometry

Arc and spark excitation techniques are very common and have been used especially in metallurgical laboratories even now. Direct current arc, which consists of a continuous discharge between a pair of metal or graphite electrodes, is beneficial for sensitive qualification in spite of relatively poor precision. Sparks, intermittent electrical discharges of a few microseconds under high electrical potentials, are used for quantification in spite of poor sensitivity because of relatively high precision. Spark source AES requires no dissolution of a sample and only applies to conductive materials, therefore it especially suits metallic samples with flat surfaces, and is utilized for daily routine analysis in industrial laboratories.

One of the great disadvantages of spark source AES is the need of reference materials that must be exactly matched as possible in concentrations of both matrixes and analytes with the samples, which is a consequence that the method has strong matrix effects and no chemical preparation can be employed. As a matter of fact, this method is significantly effective in evaluation laboratories dealing with metallic materials connected with productive lines on condition that they can afford to have working reference materials verified with the other

techniques such as ICP-AES. Of course certified reference materials commercially available are valid, but vast kinds of them must be lined up before measurement.

2.6 X-ray Fluorescence spectrometry (XRF)

Identical to the atomic spectroscopy, X-ray spectroscopy is based on the measurements of emission, absorption, and fluorescence of electromagnetic radiation as well as its scattering and diffraction. Fluorescent spectrum of elements, accompanied by an electron transition from an outer shell to an inner one of the electron orbital, is specific on wavelength, *i.e.* energy of its own. It can be detected with two types of the instrument that has a wavelength-dispersive spectrometer and an energy-dispersive one. The latter allows relatively simple design without driving units. Moreover portable and handheld instruments of this type have recently been commercially available for *in situ* analysis. XRF has a big merit that allows direct measurements by contacting the device onto materials without dissolution processes. However if quantification is needed, XRF is highly dependent on the matrixes just like the spark source AES. Furthermore it depends on the flatness, roughness and coating conditions of a sample, thus reference materials that is exactly close to the sample in concentrations of matrixes, analytes, and surface conditions are required for determination. Fundamental parameter approaches for analysis of bulk and multilayer samples without standards have been investigated, where theoretical calculation of signal intensities originated from constituent elements seems to be successful to no small extent. Although the analytical results cannot be comparable in accuracy with atomic spectrometric techniques followed by dissolution, rough determination of metallic constituents in materials and identification of alloys are considered to be available using the fundamental parameter method.

3 Analytical procedures with ICP-AES

3.1 Concept of the testing and protocol

The analytical method to be proposed as a standard seems to be acceptable for practical technicians with various environments and skills because a committee for drafting standard methods must consists of the interested manufacturers and users of the material, and also independent staffs as advisers; namely, the standard method should be held in common between manufacturers, distributors, users, consumers, and researchers. In this study, prerequisites for the methods were concluded as follows: the methods involving experienced handling, such as separation and concentration procedure should be avoided as much as possible; commercial ICP-AES instruments are almost suitable for measurements in this method; reagents and glassware are commercially available and easily obtainable among laboratories; the methods satisfy routine analysis requirements. Therefore procedures involving simple dissolution with acids and volumetric preparation, sample nebulization, and matrix matched assay standards for calibration were developed as a protocol for the tests. On the other hand, details on pretreatment operations were left to the various styles of the participants.

3.2 Interlaboratory testing

The participants concerning the testing were technical staff members belonging to chemical laboratories of the organizations in Japan, organizations that make up one of the committees

of the Japan Magnesium Association. Another participant assisted in testing by spark source atomic emission spectrometry.

Two certified reference materials (CRM) and four real samples of magnesium and magnesium alloys were used. Two CRMs, a magnesium (No.C61XMgP20A) and a magnesium alloy (No.C65XMGA50) supplied as chippings, were purchased from MBH Analytical Ltd. (Barnet, England), where the latter contains *c.a.* 8 % of aluminum, 0.4 % of zinc and 0.4 % of manganese in mass fraction. One of the real alloys named 'AZ91D' in the ASTM standard contains *c.a.* 9 % of aluminum, 0.7 % of zinc, and 0.3 % of manganese. Another one, 'AM60B', contains 6 % of aluminum and 0.4 % of manganese. All of the real samples were prepared by one of the participants, where the ingots were bored with drills and the drilled pieces were separately packed and sealed under an airtight condition using argon gas, which had *ca.* 20 g in mass per bag to be sent to the participants as test samples. The participants were requested to determine tin and lead in these samples by a following protocol of the analyses. In a second test they were requested to determine cadmium and beryllium by a similar protocol. The calibration procedure with matrix matching must be made using high-pure magnesium oxide with 99.99% (Kanto Chemicals, Tokyo), aluminum, and zinc. The analytical results must be reported as an average of the individually duplicate or triplicate runs.

The interlaboratory testing for determination of tin and lead had three series, the first of which is to check the validity of a protocol using the CRM and following determination of a real magnesium sample. The second series was to optimize matrix concentration of the sample solutions, which is indispensable to achieve for sample nebulization. Three matrix concentrations of 1, 2, and 4 % were prepared and measured separately. The last one was used to analyze real magnesium alloys with a matrix matching procedure under the optimized concentration.

All reagents used were of analytical grade or further highly purified grade, which were commercially available, and used without special designation.

Participants in eight organizations totally used nine ICP-AES equipments with eight different types in the testing, as shown in Table 3. Several different characteristics listed in the Table were useful in this study, considering that the standard methods to be constructed must be suitable for various types of equipments.

Model	Vendor	Viewing position	Nebulizer	Spray chamber	Spectrometer	Detector
(ICP-AES)						
PS-1000UV	LeemanLabs.	Radial	Hildebrand Grid	Scott	Echelle+Prism	PMT
SPS-1700HVR	Seiko	Radial	Concentric	Scott	Monochrometer	PMT
SPS1500VR	Seiko	Radial	Concentric	Scott	Monochrometer	PMT
SPS3000	Seiko	Radial	Concentric	Cyclonic	Monochrometer	PMT
SPS4000	Seiko	Radial	Concentric	Scott	Monochrometer	PMT
SPS7800	Seiko	Radial	Concentric	Scott	Monochrometer	PMT
Vista-MPX	Varian	Axial	Concentric	Cyclonic	Echelle+Prism	CCD
Vista-Pro	Varian	Axial	Concentric	Cyclonic	Echelle+Prism	CCD
(Spark Source AES)						
PDA-5500 II	Shimadzu	-	-	-	Polychromator	PMT

Table 3. Instruments of ICP-AES and Spark AES used in the interlaboratory testing

3.3 Protocol for the testing

A protocol for the dissolution of a sample as preparation was documented as follows:

1. One gram of a sample was weighed to a digit of 0.1mg and transferred to a borosilicate beaker of an appropriate size (200~300 cm^3).
2. Concentric nitric and hydrochloric acids of high purity were diluted twice with water, respectively, to make their stock solutions, *i.e.* 6.0 mol dm^{-3} of hydrochloric acid and 6.8 mol dm^{-3} of nitric acid.
3. Water as well as the twice-diluted nitric and hydrochloric acid solutions were poured into a beaker, which was subsequently covered with a watch glass, and the sample was dissolved through conventional heating after a vigorous reaction with the evolution of nitrogen dioxide gas. The dissolution process was gentle on heating so as to suppress the volatilization of acids.
4. The sample was prepared to a solution to 50 cm^3 with a volumetric flask, which contained a matrix concentration of 2 %.
5. The prepared solutions were made to finally have 0.4 mol dm^{-3} of nitric acid and 0.1 mol dm^{-3} of hydrochloric acid. The volumes and orders of the acids to be added are up to the participants.
6. To weigh 2 g of a sample and to prepare a solution to 100 cm^3 was also acceptable as an alternative operation.
7. A sample had to be pretreated in duplicate or triplicate runs.

In the second series, the above-mentioned protocol was modified so as to prepare sample solutions of 4%, *i.e.* 2 g (4 g) of a sample was weighed to dissolve and prepare a solution of 50 cm^3 (100 cm^3), thereby allowing subsequent dilution to those of 2 and 1 %.

A protocol for the preparation of standard solutions was documented as follows:

1. Magnesium oxide (99.99 % or higher in purity) was dissolved with a nitric acid solution, to prepare a 4 % solution of magnesium(II) in 0.4 mol dm^{-3} of nitric acid and 0.1 mol dm^{-3} of hydrochloric acid.
2. Aluminum (99.99 % or higher in purity) was dissolved with the nitric and hydrochloric acid solutions by five to one in volume, to prepare 0.36 % solution of aluminum(III) in 0.5 mol dm^{-3} of nitric acid.
3. Zinc (99.99 % or higher in purity) was dissolved with the nitric acid solutions, to prepare a 0.1 % solution of zinc(II) in 0.5 mol dm^{-3} of nitric acid.
4. A series of standard assay solutions of tin and lead having concentrations of 0, 0.5, and 1.0 µg cm^{-3} for metal samples and 0, 1.0, and 2.0 µg cm^{-3} for alloy ones were prepared, by diluting commercially available 1 mg cm^{-3} standard solutions of the metals or their solutions of the same concentrations prepared by dissolving high pure metals. Another series of cadmium and beryllium of 0, 0.5, and 1.0 µg cm^{-3} were prepared separately for the second test. The concentrations of matrix components had to be identical with the samples, by diluting the stock solutions of the elements as stated: Mg 2 % (unalloyed metal), Mg 1.8 %-Al 0.18 %- Zn 0.02 % (AZ91D alloy), Mg 1.88 % -Al 0.12 % (AZ60B alloy). The calibration ranges could vary appropriately according to the contents of the samples.

A Protocol for a measurement with ICP-AES was documented as follows:

The sample solutions were nebulized to be introduced directly into the plasma. Atomic emission spectra, free from spectral interferences, should be visually identified at two affordable wavelengths, where the background wavelengths are pointed out at both ends of each peak. After introducing the assay standard solutions to make a calibration line, the

sample solutions are aspirated. If repeated measurements (usually in triplicate) showed a descending tendency, the sample and standard solutions had to be prepared with an internal standard element, such as cobalt(II), thus suppressing the influence of any clogging at the orifice of a nebulizer.

4. Results of the interlaboratory testing

4.1 Results of tin and lead in the testing

Table 4 gives results of interlaboratory testing in the first series, analytical values of tin and lead of the CRM, magnesium. Each laboratory reported average values of independent duplicate or triplicate runs with adequate repeatability. The data by different analysts, dates, or equipment in the same laboratory were regarded as independent data sources. Fairly good accuracy, *i.e.* trueness and precision, was achieved by comparing the average values with the certified values of the CRM and the standard deviations with their uncertainties, respectively. Moreover, comparable data with spark source atomic emission spectrometry using an identical CRM supplied as a disk could be obtained to show that the concentration of tin and lead were 71 and 59 $\mu g\ g^{-1}$, respectively, which confirmed the accuracy of the data and the validity of the protocol.

Data No.	C_{Sn}	C_{Pb}
1	70	55
2	74	57
3	68	56
4	70	52
5	81	59
6	72	57
Average	**73**	**56**
SD	**4.6**	**2.4**
RSD, %	**6.4**	**4.2**
n	6	6
95% confidence interval	4.9	2.5
Certified values	**73**	**61**
Uncertainty[a]	**6**	**7**

Unit: $\mu g\ g^{-1}$

a. Noted in the certificate as the 95% confidence interval derived from the analysis results

Table 4. Tin and lead concentrations in the certified reference material of magnesium as the interlaboratory testing

Table 5 gives the effect of the matrix concentrations and the type of nebulizers, as well as the results in the second series of testing. The decreased number of available data is due to not only troublesome operations, but also the fact that the nebulizers for high salt concentrations were already installed into the ICP-AES instruments in the laboratories of the participants.

				$C_{Pb}/\mu g\ g^{-1}$			
	Standard nebulizer			High salts nebulizer		
	C_{Mg} ,%			C_{Mg} ,%		
Data No.	1	2	4	1	2	4
1	4.0	4.7	4.7	6.0	6.3	6.0
2	6.0	6.7	7.3	5.3	7.3	6.7
3	—	—	—	6.0	5.1	4.0
4	—	—	—	5.8	5.7	5.7
Average	5.0	5.7	6.0	5.8	6.1	5.6
SD	1.4	1.4	1.9	0.3	1.0	1.1
RSD, %	28	25	31	5	16	20
n	2	2	2	4	4	4

Table 5. Effect of matrix concentrations and type of nebulizers on lead concentrations in the real sample of magnesium

The data of No.1 and No.2 could be compared in detail, as shown in Table 6. In the former, concentric nebulizers of standard ('TR-30-A2') and high salts ('TR-30-C2') made by Meinhard Glass Products (Colorado, USA) and SPS4000 were used for measurements. In the latter, those of standard ('Conical') and high salts ('SeaSpray') made by Glass Expansion (West Melbourne, Australia) and Vista-Pro were used. In both Tables, the data seem to be independent of the matrix concentrations, but their precision obtained using nebulizers for high salt concentrations was better than those using standard ones. It is noteworthy to mention that there occurred a certain type of damage onto the outer tube and clogging of the inner tube in a plasma torch due to the introduction of solutions of 4 % for hours, especially into a horizontally aligned torch for axial viewing. Solutions of 1 % may have had insufficient emission peaks on insensitive instruments. Hence, the preparation of a sample solution to a matrix concentration of 2 % and measurements using nebulizers for high salt concentrations were considered to be preferable. Besides, another type of nebulizers for high salt concentrations, named Hildebrand grid nebulizer (Teledyne Leeman Labs., New Hampshire, USA) is also available.

Table 7 gives the results of interlaboratory testing in the first and third series on the real samples of magnesium and magnesium alloys, which were also average values of independent duplicate or triplicate runs with severally adequate repeatability. In the third series, a concentric nebulizer for high salt concentrations, 'SeaSpray' nebulizer was distributed to each participant in advance for acquiring better precision. Slight atomic emission peaks could only be observed for measurements of tin in all the real samples, which led to determinations with poor precision. But the results were adequate as JIS standards because the corresponding material standards describe upper limits of 50 $\mu g\ g^{-1}$ for tin. The concentrations of lead in the samples were fairly good on reproducibility, as shown in the table. Although some more information on reliability may well be reported as measurement uncertainty, validity of the protocol using the CRM and dispersive characteristics expressed as standard deviations were separately taken into account for discussion. The reasons are as follows: many practical problems about measurement uncertainty encountered by accredited testing laboratories have been claimed; (Visser, 2004) the participants in industry were reluctant to make use of the available measurement uncertainties owing to their unfamiliarity. Also, the reproducibility of the analytical data

used in this study is one of the major factors that contribute to the total measurement uncertainty, considering that the analytical data coincided well with their certified values.

Matrix concentration, %	Run	C_{Pb} / $\mu g\ g^{-1}$	
		Type of nebulizer	
		Standard ('TR-30-A2')	High salts ('TR-30-C2')
1	1st	5	5
	2nd	4	6
	3rd	3	7
	Average	4.0	6.0
	SD	1.0	1.0
	RSD, %	25	17
2	1st	5	6
	2nd	4	7
	3rd	5	6
	Average	4.7	6.3
	SD	0.6	0.6
	RSD, %	12	9
4	1st	5	6
	2nd	4	6
	3rd	5	6
	Average	4.7	6.0
	SD	0.6	0.0
	RSD, %	12	0

a. Meinhard nebulizers of standard ("TR-30-A2") and high salt concentrations ("TR-30-C2") and ICP-AES (SPS-4000) were used (data No.1 in Table 5)

Matrix concentration, %	Run	C_{Pb} / $\mu g\ g^{-1}$	
		Type of nebulizer	
		Standard ('Conikal')	High salts('SeaSpray')
1	1st	6	6
	2nd	7	5
	3rd	5	5
	Average	6.0	5.3
	SD	1.0	0.6
	RSD, %	17	11
2	1st	6	8
	2nd	8	8
	3rd	6	6
	Average	6.7	7.3
	SD	1.2	1.2
	RSD, %	17	16
4	1st	6	7
	2nd	8	7
	3rd	8	6
	Average	7.3	6.7
	SD	1.2	0.6
	RSD, %	16	9

b. Glass Expansion nebulizers of standard ("Conikal") and high salt concentrations ("SeaSpray") and ICP-AES (Vista-Pro) were used (data No.2 in Table 5)

Table 6. Effect of matrix concentrations and type of nebulizers on lead concentrations in the real sample of magnesium

Data No.	Unalloyed Mg		'AZ91D' alloy [a]		'AM60B' alloy [b]	
	Sn	Pb	Sn	Pb	Sn	Pb
1	2	7.5	4	44	0	9
2	—	—	5	39	-1 [c]	10
3	0.5	6.5	1	44	0	11
4	1	5	<1	53	<1	11
5	<1	2 [c]	<1	53	<1	12
6	3.1	9.7	1.4	41	2.5	10
7	—	—	2	40	1	8
8	—	—	2	41	1	9
9	1	6	2	41	1	9
10	1	6	—	—	—	—
Average	**1.6**	**6.8**	**2.5**	**44**	**0.9**	**9.9**
SD	**1.0**	**1.6**	**1.5**	**5.4**	**0.9**	**1.3**
RSD, %	**59**	**24**	**59**	**12**	**100**	**13**
n	6	6	7	9	6	9

Unit: µg g^{-1}.

a. Al, 9%; Zn, 0.7%; Mn, 0.3%

b. Al, 6%; Mn, 0.4%

c. Statistically omitted.

Table 7. Tin and lead concentrations in the real samples of magnesium and magnesium alloys as the interlaboratory testing

Data No.	C_{Cd}	C_{Be}
1	36	13
2	36	13
3	36	15
4	35	12
5	36	12
6	37	12
Average	**36**	**13**
SD	**0.6**	**1.2**
RSD, %	**1.8**	**9.1**
n	6	6
95% confidence interval	0.7	1.2
Certified values	**35**	**13**
Uncertainty[a]	**3**	**1**

Unit: µg g^{-1}.

a. Noted in the certificate as the 95% confidence interval derived from the analysis results.

Table 8. Cadmium and beryllium concentrations in the certified reference material of magnesium alloy as the interlaboratory testing

The influences of some characteristics of ICP-AES listed in Table 3 concerning the analytical data were investigated by sorting these data, which revealed no significant tendency. The average values of lead in the magnesium and magnesium alloys were almost independent of the type of chambers, viewing positions, and type of detectors studied. This may be natural, but is an important fact to be confirmed for constructing standards, especially on trace determination in coexisting matrices.

4.2 Results of cadmium and beryllium in another testing

Table 8 gives the results of another separate interlaboratory testing, determination of cadmium and beryllium of the CRM, magnesium alloy. The remarks of the values in the table were almost the same as those in Table 4. Fairly good accuracy was also achieved in the case of the magnesium alloy. Cadmium and beryllium are more sensitive than tin and

Data No.	Unalloyed Mg-1		Unalloyed Mg-2		'AZ91D' alloy [a]		'AM60B' alloy [b]	
	Cd	Be	Cd	Be	Cd	Be	Cd	Be
1	0	0	0	0	0.4	8	0	11
2	0.1	0	0	0	0.5	8	0	11
3	0	0	0	0	0.6	8	0	11
4	0.1	0	0.1	0	0.6	6	0.1	4.6
5	<1	<1	<1	<1	0.6	12	<1	9
6	-0.06 [c]	-0.12 [c]	0.16	-0.05 [c]	0.6	13	4	8.5
7	0.01	0.02	0	0	0.6	11	0.06	8.6
8	<2	<0.2	<2	<0.2	<2	11	<2	8.8
9	<6	<0.1	<6	<0.1	<6	11	<6	8.6
Average	0.0	0.0	0.0	0.0	0.6	10	0.7	9.1
SD	0.1	0.0	0.1	0.0	0.1	2.3	1.6	2.1
RSD, %	-	-	-	-	14	24	234	23
n	5	5	6	5	7	9	6	9

Unit: $\mu g\ g^{-1}$.

a. Al, 9%; Zn, 0.7%; Mn, 0.3%

b. Al, 6%; Mn, 0.4%

c. Statistically omitted.

Table 9. Cadmium and beryllium concentrations in the real samples of magnesium and magnesium alloys as the interlaboratory testing

lead, therefore easier to determine with ICP-AES. Table 9 gives the results on the real samples of magnesium and magnesium alloys, where concentrations of cadmium were too low to show significant values. In most cases, beryllium is added to magnesium alloy ingots for die castings to enhance their incombustibility; hence it could be naturally determined to *ca*. 10 µg g^{-1}. Beryllium is denoted in JIS H 2222 and allowed to use as an additive element to mass fraction of 0.0005-0.0015 %, but is very toxic as well as cadmium. It should be monitored not to exceed the permissive levels in the material.

5. Standardization of the analytical methods

The protocols evaluated in the testing were acceptable for not only the participants but also whom it might concern in Japan. They were fleshed out, formatted and submitted to an analytical committee of the magnesium industry, Japan Magnesium Association, as the original drafts for JIS standards. After an interview by Japan Industrial Standards Committee (JISC), they have been revised and provided as JIS standards. The three of them (JIS H1342, 2008; JIS H1343, 2008; JIS H1344, 2010) are newly established standards with ICP-AES, while the remainder (JIS H1339, 2010) is an updated one with ICP-AES, in addition to the flame AAS already denoted in an earlier version.

In ISO, there has been a recent action for standardization of the analytical method in the material. A standard named 'determination of lead and cadmium' is now under the level of Draft International Standard (ISO/DIS 11707, 2010), where a technical comittee /subcommittee named TC79/SC5, the title of which is 'magnesium and alloys of cast and wrought magnesium', deals with this standard. The author commits himself to this standard with the achievement of the ICP-AES techniques as mentioned in this study. He has also proposed to standardize new methods for determination of another hazardous trace metals in magnesium and magnesium alloys as a future work in ISO.

6. Conclusion

This study was designed in order to obtain an analytical basis for the concerned new standard methods with ICP-AES. In order to put excellent evaluation of the materials into practice, we must continuously know much about the analytical instruments and their characteristics. Magnesium alloys will further be developed in a wider variety as special lightweight materials; moreover a forecoming 'sound material-cycle society' will require another evaluation for used materials. Material development and its analysis as evaluation should be forwarded in a body. Furthermore, international standardization must be accompanied with its advance in order to obtain better performance in production and distribution of the material.

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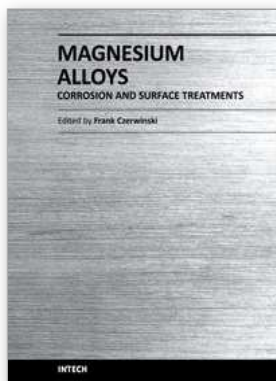
Magnesium Alloys - Corrosion and Surface Treatments

Edited by Frank Czerwinski

A resistance of magnesium alloys to surface degradation is paramount for their applications in automotive, aerospace, consumer electronics and general-purpose markets. An emphasis of this book is on oxidation, corrosion and surface modifications, designed to enhance the alloy surface stability. It covers a nature of oxides grown at elevated temperatures and oxidation characteristics of selected alloys along with elements of general and electrochemical corrosion. Medical applications are considered that explore bio-compatibility of magnesium alloys. Also techniques of surface modifications, designed to improve not only corrosion resistance but also corrosion fatigue, wear and other behaviors, are described. The book represents a valuable resource for scientists and engineers from academia and industry.

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